Electroorganic Synthesis for the Conversion of Fatty Acids and Levulinic Acid into Chemicals and Alternative Fuels

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Harnisch, F., Blei, I., **Santos, T. R. d.**, Möller, M., Nilges, P., Eilts, P., and Schröder, U. From the test-tube to the test-engine: assessing the suitability of prospective liquid biofuel compounds. RSC Adv., 3:9594-9605, 2013.

Nilges, P., **Santos, T. R. d.**, Harnisch, F., and Schröder, U. Electrochemistry for biofuel generation: Electrochemical conversion of levulinic acid to octane. Energy Environ. Sci., 5:5231-5235, 2012.

Tagungsbeiträge

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Santos, T. R. d., Sauter, W., Nilges, P., Harnisch, F., and Schröder, U. Electrochemistry for biofuel generation: Transformation of free fatty acids and triglycerides to a diesel-like mixture. In Electrochemistry GDCh - Tagung, Mainz, September 2014.

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Nilges, P., **Santos, T. R. d.**, Harnisch, F., and Schröder, U. Electrochemistry for biofuel generation: Electro-chemical conversion of levulinic acid to octane. In Electrochemistry 2012 - GDCh - Tagung, München, September 2012.

Abstract

The present work focuses on electroorganic synthesis for the conversion of biomass derived feedstocks into chemicals and fuels. Electroorganic syntheses entail reactions that take place at ambient temperature and pressure, and can use water as solvent. Thus two important criteria in the context of "sustainable chemical processes" assessment. With this in mind the current work investigates how electroorganic oxidation and reduction can be used for energy storage. The research of alternative fuels presents some peculiarities, especially the uncertainty regarding the requirements for prospective fuels from the chemical point of view. In this context, the present work discusses key properties for an initial fuel characterization and reinforces the importance of understanding the chemical structure of products from fossil and renewable biomass sources. This assessment aims to provide an alternative for the evaluation of the suitability of a chemical compound as fuel in an early stage research. The development of a suitable and flexible concept for the chemical analysis of the compounds involved in the electrochemical reactions is a fundamental part of the present work. The developed concept enables the evaluation of different electrochemical reactions. Lipids and levulinic acid are important products and feedstock of biorefineries, they have been therefore chosen as basis for two different electroorganic pathways investigated in this work. The first pathway has investigated the decarboxylation of fatty acids based on the non-Kolbe electrolysis It has been demonstrated that electroorganic synthesis can be exploited for the production of an olefin/ether mixture from fatty acids in organic solvents and for the production of olefins in aqueous electrolyte emulsions using sonoelectrochemistry. The second approach presents the primary and secondary conversion of levulinic acid by means of electrochemical oxidation and reduction at room temperature using water as solvent. The electrochemical conversion of levulinic acid leads to different products and present good yields, selectivities and coulomb efficiencies. The formed products may find either direct application as fuel, solvent or as intermediates for further reactions. The choice of the electrolyte composition and electrode material has shown a strong influence on the selectivity of the product formation. For some of the reactions the main product is insoluble in the electrolyte solution, which allows a direct separation of the product and the electrolyte reuse in a semi-continuous process. The use of a flow reactor is a important step for the upscaling, but for the investigation of unknown reactions it still presents some limitations. A comparison of the electric energy input with the heating values of the products on the example the decarboxylation of long chain fatty acids indicates that electroorganic conversion may provide an interesting and potentially energetically competitive process.

Kurzfassung

Die vorliegende Arbeit fokussiert sich auf elektroorganische Synthesen für die Umwandlung biogener Plattformchemikalien in Chemikalien und Kraftstoffe. Elektroorganische Synthese ermöglicht Reaktionen bei Raumtemperatur und Normaldruck, sowie die Verwendung von Wasser als Lösungsmittel und erfüllt somit wichtige Kriterien der grünen Chemie. In diesem Zusammenhang wird untersucht, wie elektroorganische Oxidation und Reduktion zur Energiespeicherung eingesetzt werden kann und welche Produkte erzielt werden können. Bei der Untersuchung alternativer Herstellungsverfahren regenerativer Kraftstoffe müssen die Anforderungen an zukünftige Kraftstoffe analysiert und berücksichtigt werden. In diesem Kontext werden in dieser Arbeit Schlüsseleigenschaften für eine erste Kraftstoffcharakterisierung und die Bedeutung des Verständnisses der chemischen Struktur von Produkten fossiler und biogener Herkunft beschrieben. Diese Darstellung soll eine Alternative für die Bewertung der Eignung einer chemischen Verbindung als Kraftstoff in einem frühen Stadium der Forschung bereitstellen. Die Entwicklung eines geeigneten und flexiblen Konzepts für die chemische Analyse der in den elektrochemischen Reaktionen beteiligten Verbindungen ist ein wichtiger Bestandteil der vorliegenden Arbeit. Das entwickelte Konzept ermöglicht die Bewertung der verschiedenen elektrochemischen Reaktionen. Lipide und Lävulinsäure sind wichtige Bioraffinerieprodukte, daher wurden sie als Grundlage für zwei unterschiedliche Ansätze in dieser Arbeit gewählt. Der erste Weg ist die Decarboxylierung von Fettsäuren, mittels non-Kolbe Elektrolyse. Es konnte gezeigt werden, dass die elektroorganische Synthese für die Herstellung eines Olefin / Ether-Gemisch aus Fettsäuren in organischen Lösungsmitteln und für die Produktion von Olefinen in wässrigen Elektrolyten mit Hilfe von Ultraschall angewendet werden kann. Der zweite Ansatz stellt die primäre und sekundäre Umwandlung von Lävulinsäure durch elektrochemische Oxidation und Reduktion bei Raumtemperatur unter Verwendung von Wasser als Lösungsmittel dar. Die elektrochemische Umsetzung von Lävulinsäure führt zu verschiedenen Produkten und ermöglicht gute Ausbeuten, Selektivitäten und Coulombsche Effizienz. Die gebildeten Produkte können entweder direkt Anwendung als Kraftstoff, Lösungsmittel oder als Zwischenprodukte für weitere Reaktionen finden. Die Wahl der Zusammensetzung des Elektrolyten und Elektrodenmaterial zeigt dabei einen starken Einfluss auf die Selektivität der Produktbildung. Bei einigen Reaktionen ist das Hauptprodukt in der Elektrolytlösung schwer l□slich. Dies ermöglicht eine direkte Trennung des Produkts und die Wiederverwendung des Elektrolyten in einem halbkontinuierlichen Verfahren. Die Verwendung eines Durchflussreaktors ist ein wichtiger Schritt für das Scale-up, aber für die Untersuchung unbekannte Reaktionen sind noch Einschränkungen vorhanden. Die energetische Betrachtung der durchgeführten Reaktionen zeigt, dass die elektroorganischen Umwandlung einen konkurrenzfähigen Prozess aufweisen kann.

An dieser Stelle bedanke ich mich ganz herzlich bei all jenen Personen, die mir bei dem Erstellen dieser Arbeit zur Seite gestanden haben. Ihre stetige Unterstützung haben dieser Arbeit erst möglich gemacht.

Contents

1 | Introduction

The development of a sustainable chemical industry, including the fuel production, depends on biomass and the replacement of the current petroleum based production pathways. For the implementation of new processes and products, new approaches in research and development are essential. The establishment of the industry of the future depends on new synergies of biological, physical, chemical, and technical sciences (Kamm et al. 2000).

As described in Chum and Baizer 1985, the utilization of biomass may be especially applicable to small-scale, energy efficient, and decentralized processes that are not capital-intensive. The availability of biomass resources is also obviously a function of its management. This management depends on a variety of factors including governmental policies, economy, climate, and the resulting costs of fossil-derived and biobased fuels and chemicals. The important and complex issue over the utilization of biomass — the food versus fuel controversy — was not in the scope of this thesis .

Biorefinery products (energy, chemicals and materials) should be integrated into existing petroleum-derived products. But the integration is not always simple, considering several differences between these two pathways. The comparison listed in Table 1.1 gives an overview on the challenges and opportunities upcoming with the combination of biorefineries to conventional petrorefineries (Clark and Deswarte 2008).

Biofuels represent one of the main pillars of bioeconomy and their production/consumption has experienced a rapid growth in the past years. This trend is forecasted to continue, and an even further doubling can be expected (Scheffran 2010). Nevertheless, such widespread use of biofuels depends on the development of new process technologies for the production of high quality fuels from different feedstocks (Kalnes et al. 2007). Although it has so far not been applied for biofuel production purposes in industrial scale, electroorganic chemistry may offer a great potential in the sustainable production of fuels and chemicals from biomass. Furthermore, electrochemical methods may allow a small scale, and thus decentralized, operation at comparable low investment costs, representing an important step for the establishment of ”power-to-gas” and ”power-to-liquid” technology.

Table 1.1: Comparison of petrorefinery and biorefinery in terms of feedstock, conversion processes and products (CLARK and DESWARTE 2008, pp. 14)

	Petrorefinery	Biorefinery
Feedstock:		
Location	Rich deposits in some areas	Widely distribuited
Density	High	Low
Availavility	Continuous but finite	Seasonal but renewable
Chemical composition	Hydrocarbons, not funcionalised	High oxygenated and funcionalised
Conversion processes:	Optimised over 100 years	Require further research and technological development
Products:	On the market and to high specification	Quality needs to be standardized, low market shares

The electrochemical syntheses, and the upgrading of biological feedstocks and derived compounds may provide a promising pathway to gain novel biofuels (SCHÄFER 2012; WALDVOGEL and JANZA 2014). However, beside its obvious advantages these methods are largely unexplored at industrial scale.

1.1 Objective

The focus of this work was the investigation of electrochemical synthesis for the synthesis and upgrading of biomass derived compounds, in the frame of the development of a new alternative concept of sustainable biomass conversion. A major goal of this thesis was the demonstration of electroorganic synthesis for the transformation of long chain fatty acids, present in fats and oils, into liquid fuels as an alternative to the often problematic biodiesel (Chapter 2). This is of special importance as fats and oils already represent a currently exploited feedstock and thus the material base and related infrastructure are already present. Furthermore, the electrochemical upgrading of levulinic acid (a molecule obtained from the hydrothermal treatment of carbohydrate-rich biomasses) was investigated.

Since tests regarding the applicability of biomass based compounds as prospective (bio)fuel based on small quantities (in mL range) are not usual, and in some cases not even possible, an alternative assessment has been proposed in order to provide a suitability evaluation even before the beginning of lab experiments. For this purpose, an evaluation of key parameters allowing an initial characterization of diesel-like fuels is discussed in this work and some of these parameters are applied for the energetic considerations related to the electrochemical conversion.

Basic energetic considerations for both studied precursors (fatty acid and levulinic acid) were presented in order to illustrate the feasibility of electroorganic synthesis for biofuel

production as well as for the storage of electric energy.

Summarizing, this work aims to combine the application of electricity for the operation of chemical reactions and the use of renewable biomass products.

1.2 Outline

Figure 1.1 illustrates the interaction of the different topics studied on this work.

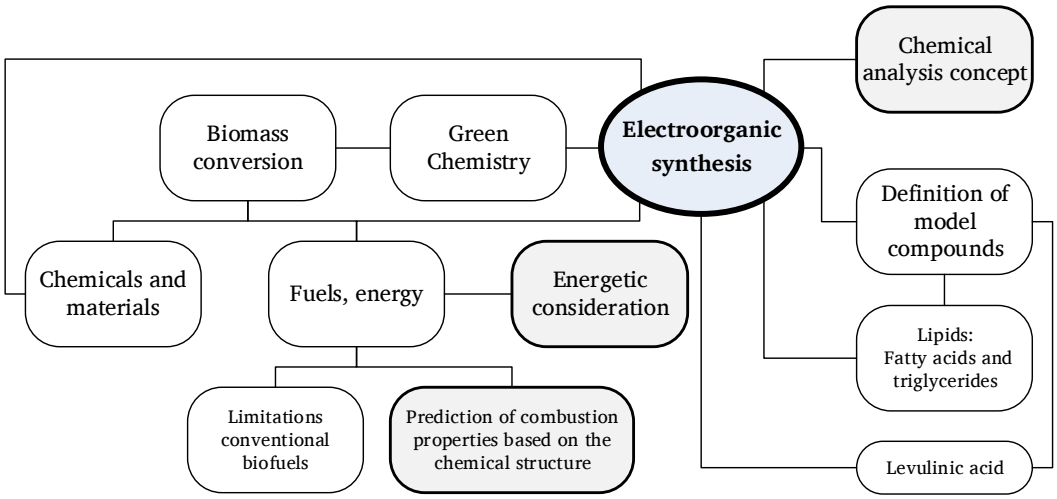

Figure 1.1: Overview of the major topics and issues that were the basis for the present work

Chapter 2 presents an overview of organic electrochemistry in the context of biomass conversion. The methods of conventional biofuel production will be briefly described. Chapter 3 discusses selected key properties allowing an initial characterization of diesel-like fuels. Chapter 4.1 outlines the chemical analytical methods applied for the evaluation of the different electrochemical reactions. Chapter 4.2 describes the electrochemical procedures, set-up and main parameters. In Chapter 5 an approach for primary and secondary conversion of levulinic acid by means of electrochemical oxidation and reduction is presented and selected reactions were tested in a flow set-up. Chapter 6 demonstrates that fatty acids an triglycerides can be electrochemically converted for the production of diesel-like olefin/ether mixtures. In Chapter 7 the energetic considerations regarding the electroorganic synthesis and its potential as energy storage method are presented. Finally, the conclusions are drawn in Chapter 8.

2 | Context

Some of the terms used in this interdisciplinary field are used in different contexts. Therefore, a short definition of these terms in the context of this thesis shall be given.

Green Chemistry: following a succinct definition according to Sheldon 2014: "green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous solvents and reagents in the manufacture and application of chemical products".

Biomass and Industrial biomass: there are several definitions of the term "biomass", but in context of this work, the definition of "industrial biomass" is more relevant and the definition from Kamm et al. 2000 will be followed: "The term industrial biomass means any organic matter that is available on a renewable or recurring basis (excluding old-growth timber), including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes, and other waste materials usable for industrial purposes (energy, fuels, chemicals, materials) and include wastes and co-wastes of food and feed processing".

Biofuel: within this work biofuel is defined as "liquid substances, derived from renewable biomass resources, serving as a pure substance or within a complex mixture as automotive fuel in combustion engines" (Harnisch et al. 2013).

Electrofuel: within this work electrofuel is defined as suggested by Ridjan et al. 2015 "fuels produced by storing electricity as chemical energy in the form of liquid or gas substances".

2.1 Biomass, Derived Materials and Green Chemistry

Biomass, similar to petroleum, has a complex composition, each with a specific composition. Therefore, the separation of the biomass derived compounds into main groups of substances is helpful (Kamm et al. 2000). Detailed information about biomass composition and the biorefinery concept can be found in Kamm et al. 2000 and also in the comprehensive review from Alonso et al. 2010. The most important classes of feedstocks derived from biomass are:

carbohydrates, triglyceride and lignocellulosic (Alonso et al. 2010). The compounds derived from these substances are termed platform chemicals. Since biogenic platform chemicals are highly oxygenated and the energy density decreases with the oxygen content in the molecule, the transformation of these molecules to low oxygenated products, via reactions as dehydrogenation, hydrogenolysis, hydrogenation, decarbonylation/decarboxylation is a fundamental step for the application of these compounds as fuels. Commonly, all target reactions (see Figure 2.1 for selected examples) involve the increase of the specific energy per mass unit in order to make the molecule more suitable as biofuel.

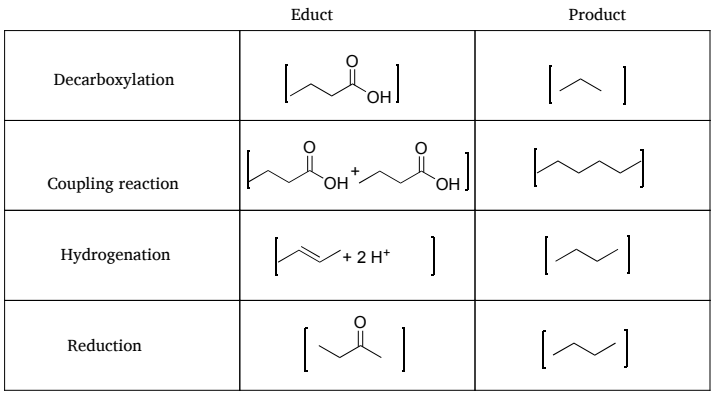

Figure 2.1: Electrochemical target reactions for the increase of the specific energy per mass unit

In addition to the reduction of the oxygen content, the C−C coupling reactions are particularly interesting for biomass derived molecules and especially for these with less than 6 carbons, when the final products are to be used as fuels in diesel engines and jets. The treatment of carbohydrate based biomasses by thermal processes, including subcritical water processing, yields numerous compounds that cannot be directly used as biofuel or as platform chemicals (Möller et al. 2011). These compounds include carboxylic acids (e.g. formic acid, lactic acid and levulinic acid), aldehydes (e.g. formaldehyde) and alcohols as well as furan and its derivatives, most prominently 5-hydroxymethyl-furfural (Möller et al. 2011).

Although the share of triglycerides feedstocks is far smaller than those of lignocellulosic biomass, their relevance can not be neglected. Fats and oils represent high-energy storage substance of plants, animals and microorganisms (Lestari et al. 2009), making their exploitation for the production of chemicals and biofuels a very appealing goal e.g Biermann et al. 2011; Schäfer 2012).

As described in Kamm et al. 2000, the development of systematic approaches to new syntheses and technologies is required to meet the sustainable principles of “ideal synthesis” and “principles of green chemistry and process engineering” . Furthermore, the envisaged use of fuels from biomass depends on the development of new technologies for their pro-

duction (Kalnes et al. 2007). Nevertheless, the development of new concepts does not exclude the exploration of old reactions with appropriate adjustments to the current requirements of green chemistry. In this light, electroorganic syntheses, obeying the rules of green chemistry, currently experience a renaissance (Waldvogel and Janza 2014) as they offer a great potential for the sustainable production of fuels and chemicals from biomass. This potential, for instance, has recently been demostrated on the examples of the production of vanilin from black water (Stecker et al. 2014) or the conversion of levulinic acid and furfurals (Nilges et al. 2012; Nilges and Schröder 2013).

The next sections provide an overview of the two main platform chemical groups studied in this work, as well as the current methods and the possibilities of electrochemical synthesis.

2.2 Conventional Biofuels

Historically, during petroleum shortages, vegetable oils and their derivatives have been proposed as alternatives to petroleum diesel fuel. However, only a limited number of biofuel types have already been introduced in the market, most prominently bioethanol, *i.e* ethanol from sugar cane or wheat (Hansen et al. 2005), and biodiesel, *i.e* fatty acid methly-esters (FAME) or fatty acid ethyl-esters (FAEE) derived from plant oils and fat (Atsumi and Connor 2010; Demirbas 2010; Narasimharao et al. 2007).

Until now, a large share of the fat and oil derived biofuels are produced via transesterification (Meher et al. 2006) resulting in FAME and FAEE (Encinar et al. 2012) — both often denominated “biodiesel” and together being the worldwide second most exploited renewable automotive fuel. However, biodiesel has drawbacks like: poor cold flow properties, low oxidative stability (Knothe 2011), high boiling temperature and especially corrosivity. The latter is due to the hydrolytic instability of the ester-bonds resulting in the formation of free fatty acids (Bondioli et al. 1995). To reduce these drawbacks it is desirable to convert fats and oils into hydrolytically stable compounds with a lower boiling point, such as alkanes, olefins and alkyl-ethers.

An alternative route to the transesterification process is the hydrotreating/ hydroprocessing of triglycerides which yields liquid alkanes — “green diesel”, that are suitable for diesel and jet fuel applications (Kubičková and Kubička 2010). However, these processes require hydrogen at high pressures and temperatures (Serrano-Ruiz et al. 2012) incurring in lower energy efficiency and additionally not being easily applicable in decentralized processes. These limitations have motivated the search for new approaches to the production of high energy density biofuels (advanced biofuels) compatible with the present transportation infrastructure Climent et al. 2014.

As a consequence of the recent debate on the impact of biofuel oriented biomass utilization

and arable land consumption on the food production (Escobar et al. 2009; Pimentel et al. 2009), lignocellulose has become a major target as a future commodity for biofuel and chemical feedstock production (G. Cassman and Liska 2007). Research and development of lignocellulose based production routes is nowadays characterized by a high diversity concerning the potential pathway and the stage of developments as well as its final products (Chheda et al. 2007; Huber et al. 2006). Consequently, the diversification of primary raw materials for renewable transportation fuels, including an array of waste materials (in the biorefinery context considered an obsolete term) is expected to come into place future (Hansen et al. 2010).

2.2.1 Properties of Prospective Biofuels in the Context of their Chemical Structure

Beside the economical, ecological and socio-political advantages and disadvantages of conventional methods (Zinoviev et al. 2010) it has to be noticed that the product spectrum, *i.e.* chemical compounds that are proposed as prospective biofuels, is highly diverse (see *e.g.* (Chheda et al. 2007; Huber et al. 2006). In this course, except the chemical compounds are found in today's petro-chemical fuels, the automotive suitability of prospective biofuel molecules (like n-butanol) often remains a matter of speculation.

Up to now, only fuel characterizations in test-engines or respective pre-experiments, *e.g* in spray chambers, provide adequate information on the suitability of a certain fuel (Groth and Hesse 1985). However, from the chemist's perspective these assessments require comparative large fuel quantities (*e.g* several hundred mL) for spray chamber tests and more than 1 L for test engines, (Azev et al. 1978). These biofuels quantities are generally not available from lab-bench experiments — often yielding only several mL or mg. As a consequence, key parameters must be defined for lab-based methods in order to assess the suitability of a biomass derived molecule as a biofuel. Based on an evaluation of these key parameters it can be decided, if the molecule itself can be suitable as biofuel or if further chemical transformations (including, *e.g* functionalization and defunctionalization) are needed (see Chapter 3).

2.3 Electrochemical Conversion of Biomass Derived Chemicals

Electrochemical conversion consists on the application of an electric potential between, two active electrodes, resulting in oxidation and reduction and thus to a flow of current. These reactions have been studied extensively in the past, so that nowdays the challenge regarding this kind of synthesis consists much more in finding new concepts and tools to analyse and optimize their impact according to the "green (electro)chemistry" context. Since the

electrooganic synthesis has to compete with established methods (*e.g.* heterogeneous and homogeneous catalysis), as well as with emerging processes (*e.g.* enzymatic catalysis, photocatalysis), innovative concepts have to demostrate their competitiveness and flexibility as early as possible (MATTHEWS 2001).

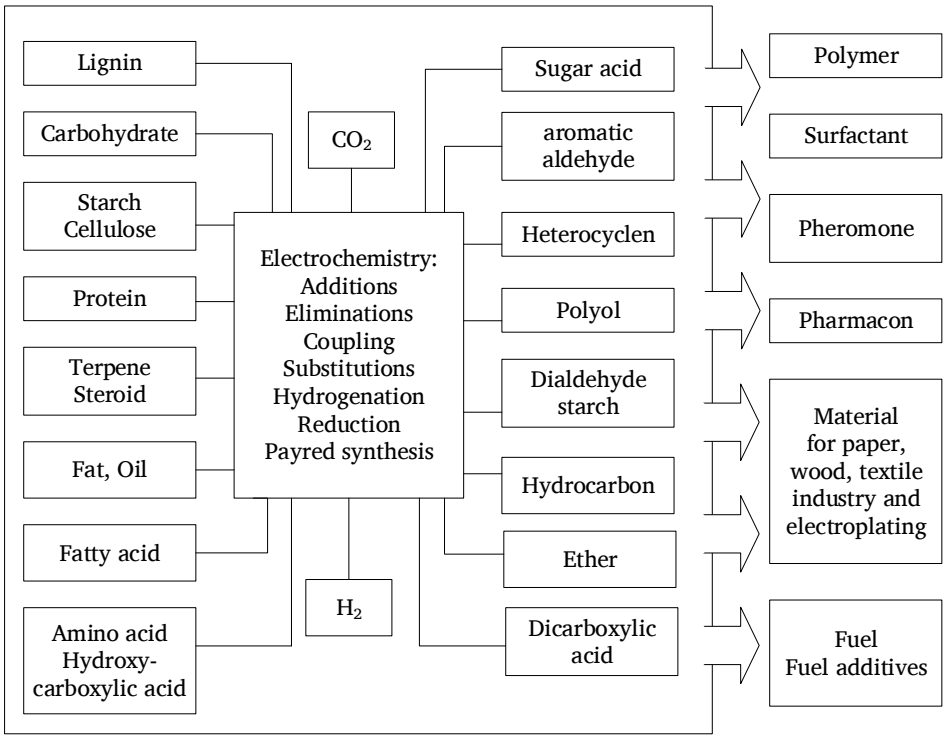

Figure 2.2: Alternative and renewable material electroorganic synthesis providing potential feedstocks for the chemical industry and energy production (adapted from *Industrielle Organische Elektrochemie* 2006)

An important positive aspect of electrochemical synthesis is their potential to fulfill at least six (SCHÄFER et al. 2007) of the 12 criteria/ rules defined for "sustainable chemical processes" (P. T. ANASTAS and WARNER 1998) :

- the use of the "immaterial" reagent electron which results in the avoidance of waste;
- the final product incorporate the majority of materials used in the process (atom economy);
- the replacement of toxic oxidants and/or reductants, which results in a minimization of hazards;
- the use of water as the preferable (and safe) solvent;
- the reactions preferentially proceed at ambient temperature and pressure;
- and the exploitation of renewable feedstocks (complex mixtures containing e.g. carbohydrates) as shown in Figure 2.2.

2.3.1 Levulinic Acid

Levulinic acid (LA), produced from lignocellulosic biomass, is considered to be an important precursor for renewable chemicals and liquid biofuels (Bozell and G. R. Petersen 2010; Serrano-Ruiz et al. 2010b; Werpy and G. Petersen 2004). The synthesis of levulinic acid from saccharose was reported already in 1840 (Mulder 1840) and since the 1970s many of its reactions were established and studied from different perspectives. Until now it has not reached commercial use in significant volume, but it is still considered as a platform chemical with a high potential for the production of fuels and chemicals (Alonso et al. 2013; Kamm et al. 2000). Generally, LA can be produced in high yields from carbohydrates and from lignocelluloses by acid catalyzed hydrolysis (Chen et al. 2011; Gallezot 2012; Girisuta et al. 2008, 2007, 2006; Hegner et al. 2010; Peng et al. 2010; Shen and Wyman 2012; Szabolcs et al. 2013; Tarabanko et al. 2002; Weingarten et al. 2012).

The review by Rackemann and Doherty 2011 outlines the chemistry of levulinic acid from lignocellulosics biomass. Its molecular structure, comprising two functional groups (a keto and a carboxyl group), makes levulinic acid an ideal platform chemical (see Figure 2.3 for an overview of the proposed reactions studied in this work). The lab-scale synthesis of biochemicals, polymers, pharmaceuticals, flavor agents, solvents, antifreeze agents, biofuels, and herbicides from LA has been reported in Bozell and G. R. Petersen 2010; D. Elliott and Frye 1999; Fitzpatrick n.d.; Ghorpade and Hanna 1997; Hayes et al. 2008; Huber et al. 2006; Kitano et al. 1975; Leonard 1956 and presentend in more details in Table 2.1. The respective syntheses are generally based on homogeneous and heterogeneous catalysis, whereas electrochemical conversions of LA and derivates are only rarely described (e.g. Xin et al. 2013 and Qiu et al. 2014).

Table 2.1: Relevance of the compounds potentially derived from levulinic acid via electrochemical conversion: Application and conventional production methods

Product	Application	Conventional Synthesis
Valeric acid	Intermediate to valeric fuels and additives	The catalytic hydrogenation of levulinic acid to valeric acid typically is done in a two-step reaction at high temperature (150-350 °C), under high hydrogen pressure (10-40 bar) and at different platinum metal based catalyst (Lange 2009; Lange et al. 2010; Serrano-Ruiz et al. 2010a)
y-valerolactone (gVL)	Intermediate to butene, valeric acid, and 5-nonanone.production. gVL can be used as a solvent derived from biomass (Alonso et al. 2013)	Catalytic hydrogenation to gVL was done using different transition metal based catalyst at high temperature (70-265 °C) under hydrogen atmosphere (5-150 bar) (Alonso et al. 2013)
2,7-octandione (2,7-OD)	The occurring 2,7-octandione can be used in a intramolecular aldol reaction (Bouillon et al. 2012; Hoffmann et al. 2012) or intramolecular pinacol coupling	Usually achieved by complex catalytic routes, *e.g.*, based on Au catalyzed reaction of the di-acetylene at 120 °C (Nun et al. 2010), Ir-complex-catalyzed addition of water to 1,7-octadiyne at 70 °C (Hirabayashi et al. 2006) or the Pd catalyzed Wacker oxidation of olefins at 80 °C under oxygen (6 atm) in DMA (Mitsudome et al. 2006)
4-hydroxy-2-butanone (4H2B)	4-hydroxy-2-butanone is used as a platform chemical for further synthesis, like a dehydration to 3-buten-2-one (Ichikawa et al. 2005) as well reduction to 1,3 butanediol (Kobayashi et al. 1995) or 1-butanol (electrochemically shown below (Chapter 5))	4-hydroxy-2-butanone is industrially produced by the coupling of fossil source based propanone and formaldehyde in basic media (Hays et al. 1951). The Wacker-type oxidation of 3-buten-1-ol (Bawaked et al. 2011), selective catalytic dehydrogenation of 1,3-butanediol (Kessat et al. 2001; Sato et al. 2007; Su et al. 2006), selective heterogeneous catalytic oxidation of 1,3-butanediol with H_2O_2 in CH_3CN (Bordoloi et al. 2008; Lang et al. 2008) and reduction of a dicarbony (1,3-butanone) at 130 °C over metallocene complexes (Nakano et al. 1988) are examples for the complex formation of 4-hydroxy-2-butanone (Wang et al. 2013)
3-buten-2-one (MVK)	Used in the production of gas-tight plastics, a intermediate in the production of pharmaceutical, fungicides Jahn 2014, vitamin A und vitamin E (Eggersdorfer et al. 2000). Important compound in Michael-Additions, Robinson-Annulations, Diels-Alder-Reactions, Baylis-Hillman-Reactions, radical additions heterocycle-synthesis; often found in natural material synthesis (polyketides, macrolactone, terpenes, pheromons and alkaloids) (Jahn 2014)	Technically, 3-buten-2-one is built from acetone with formaldehyde and diethylamine hydrochloride (Mannich-reaction) or by Aldol-condensation of acetone and formaldehyde (Jahn 2014) The catalytic oxidation of levulinic acid over CuO/CeO_2 and CuO/Al_2O_3 gives 2-buten-3-one in at 175 °C (Gong et al. 2012) or at 300 °C over CuO_2 (Gong et al. 2010), it is also patent-registered (West and Dumesic 2010)
1,3-butanediol (1,3-BDO)	Polyester plasticizers, humectants	
n-octane	n-octane is used as solvent, cleaning agent, fuel additive or as reaction agent like oxidation by cobalt (Garcia-Ochoa et al. 2012) aromatization (Trakarnroek et al. 2006) is described also	Fractional distillation and refining of petroleum or the selective electrolytic reductive homocoupling of alkyl iodides at Ag-Pd cathodes in dipolare solvents (Poizot et al. 2009)
2-methyltetrahydrofuran (2-MTHF)	2-Methyltetrahydrofuran is mainly used as a higher boiling substitute for tetrahydrofuran as specially solvent. 2-MTHF can also be used in the electrolyte formulation for secondary lithium electrodes and as a component for alternative fuels (Koch and Young 1979; Al-Shaal et al. 2014)	2-MTHF is produced by Ni-catalyzed hydrogenation of 2-Methylfuran. This reaction can be performed in the liquid phase under H_2 pressures of 2 MPa or in the vapor phase at atmospheric pressure with common supported Ni catalysts (Hoydonckx et al. 2000)

2.3.1.1 Electrochemical Upgrading of Levulinic Acid

As Table 2.1 shows, most of the conventional synthesis routes for the conversion of levulinic acid are high-temperature and high-pressure processes. Electrochemical synthesis may provide an alternative route, as the respective reactions (Figure 2.3) can be carried out in aqueous solutions and at room temperature, fulfilling two major criteria of green chemistry (P. Anastas and Eghbali 2010). The electrochemical formation of γ-valerolactone (gVL) from LA was first described by Tafel and Emmert 1911, when they studied the electrochemical reduction of levulinic acid in alkaline solution at a lead cathode. Further examples are the oxidative formation of 5-acetyl-2,9-decanedione in a methanol/water solution (Cabasso et al. 2012), and recently, the works of Xin et al. 2013 and Qiu et al. 2014 reporting on electrocatalytic processing of levulinic acid to produce biofuels.

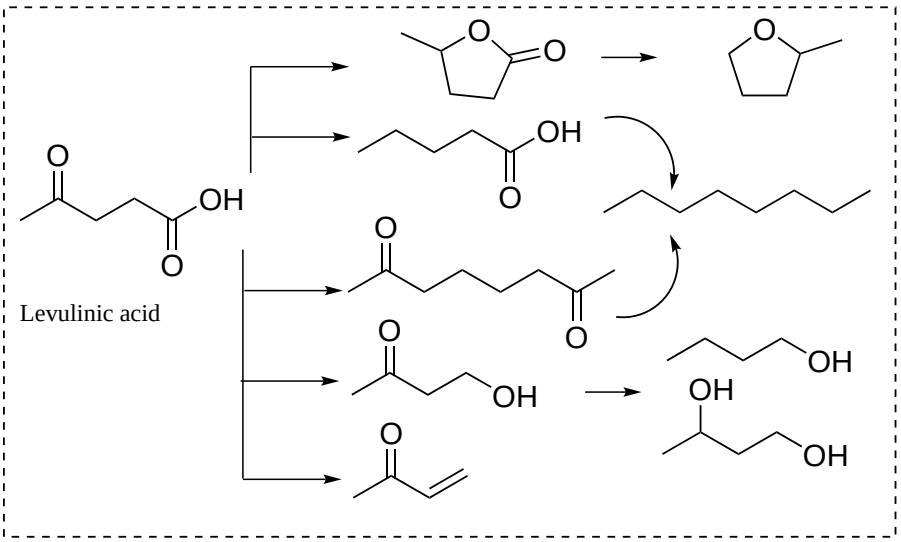

Figure 2.3: Proposed reactions pathways for levulinic acid, simplified illustration based on Figure 5.1

Additionally to the interesting product spectrum and its exploitation to (bio)chemical synthesis, the direct use of electric current for chemical conversion may even allow the storage of energy from renewable resources like wind power and photovoltaic in the form of chemical potential energy into compounds with higher energy density. For serving as a high energy density fuel molecule, oxygen functionalities have to be removed from LA, for which new processes are needed. For some of the conversions from LA to a (more reduced an thus higher energy density) target molecule, consecutive reactions, *i.e.* an oxidation followed by a reduction or vice versa, are necessary. Such a combined oxidation (at the anode) and reduction (at a cathode) can, in principle, be achieved simultaneously in only one electrochemical cell.

2.3.2 Fatty Acids and Trigycerides

Vegetable oils find many uses in industry for the production of lubricants, surfactants, soaps, surface coatings, solvents, polymers and fuel (Clark and Deswarte 2008). Triglycerides (triacylglycerols) are the main constituent of natural oils, fats and lipids. They share the common backbone molecule, glycerol, but differ significantly concerning their fatty acid composition. However, the molecular structure of the fatty acids, *i.e.* their chain length (generally C_{14} and C_{22}) and degree of saturation, as well as their binding site on glycerol determine the physical-chemical properties of respective triglyceride and triglyceride mixtures (Gunstone et al. 2007). This is shown in Table 2.2 depicting the boiling temperature/ boiling range, and the melting point of oils, lipids fatty acids and derived fuels and petrochemical diesel fuel.

Table 2.2: Comparison between boiling point and distillation ranges of diesel and vegetable oil and their products (F. Lackner et al. 2010)

starting material	**Boiling point/ boiling range / °C**	**Melting point /°C**
Diesel	180-340	-40-1
Palm oil	545	30-40
Palmitic acid	340-355	61-62.5
Methyl palmitate	351	28.5
1-Pentadecene	268-269	-4
Triolein	235-240 (24 mbar)	-5
Oleic acid	360	13-14
Methyl oleate	218(27 mbar)	-20
Ethyl oleate	210	-32
1-Heptadecene	300	10
Rapeseed oil	246 (smoke point)	-10
FAME	326-366	-3 -18
Hydrotreating - products	265-320	-10 20

During the hydrolytic cleavage of plant oils, one mol of glycerol is gained per 3 moles of fatty acids, or approximately 0.1 tons of glycerol per ton of biodiesel (Gunstone et al. 2007; Won et al. 2009). Thus, glycerol represents the main, by-product of biodiesel production and is expected to be present in the electrochemical reaction starting with triglycerides. (Gunstone et al. 2007). Glycerol contains three hydrophilic alcoholic hydroxyl groups, is a highly flexible molecule (Pagliaro and Rossi 2010), and constitutes an interesting feedstock for various C_3 commodity chemicals that are currently produced in petrochemical processes from propylene (Sheldon 2014). An overview about the upgrading of glycerol to commodity chemicals can be found at Pagliaro and Rossi 2010. The electrochemical oxidation of glycerol is only one of the many examples for the conversion of glycerol into high value added compounds (Hunsom and Saila 2015). The oxygenates of glycerol present a high economical relevance (Pagliaro et al. 2007), *e.g.* dihydroxy−acetone (DHA), which electro-

chemical conversion has already been described, it is used in the cosmetic and chemical industry, where further derivatives may play an important role in building blocks for fine and polymer chemicals (PUTNAM and ZELIKIN 2005).

2.3.2.1 Electrochemical Upgrading of Fatty Acids

Fatty acids contain different electroactive groups, such as the carboxyl group, the double bond and the allylic C–H bond (SCHÄFER 2012). During the oxidation of the carboxyl group, hydrocarbon radicals (C_n*) are formed, which can react further and form dimers (C_n-C_n), by a one electron pathway (Kolbe-reaction), or monomers (C_n-H), by a two electron reaction (Non-Kolbe-reaction/ Hofer-Moest-reaction), as depicted in Figure 2.4. These are among the oldest known electroorganic reactions (H. HOFER and MOEST 1902; KOLBE 1849). To date, the electrochemical conversion of long-chain carboxylic acid has been demonstrated only for the Kolbe reaction, yielding dimer products with chain lengths above C_{30} (i.e. paraffins) (WEIPER and SCHÄFER 1990). These compounds possess a boiling point above 450°C (Table 2.2) and thus are unsuitable for biofuel applications. The electrochemical transformation of fatty acids via non-Kolbe reaction in organic solvent, yielding C_{15} to C_{20}-alkenes, i.e. olefins, and ethers has so far only been reported once without any detailed information (BUSCH 2008).

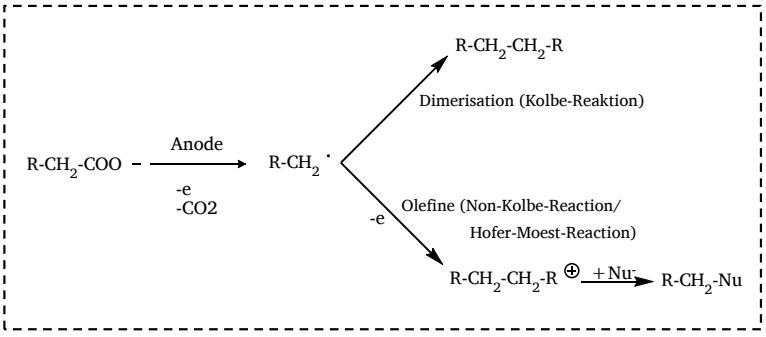

Figure 2.4: Example of anodic decarboxylation via two electron reaction and ether formation with the respective alcohol

As SHELDON 2014 emphasizes: "the best solvent is no solvent but if a solvent cannot be avoided it should be safe to use and there should be provisions for its efficient separation from the product and reuse" . This has stimulated extensive studies, over the last two decades, of non-conventional reaction media such as water, supercritical CO_2 and ionic liquids. Thus, from the standpoint of green chemistry the use of an aqueous electrolyte solution is a clear advantage over organic solvents (P. T. ANASTAS and WARNER 1998). Since oils, fats and fatty acids are only sparingly soluble in aqueous solutions, sonoelectrochemistry has been proposed to produce emulsion for electrochemical decarboxylation. Previous studies on

the oxidation of emulsions of water-immiscible short chain organic acids (R-CO_2H), such as hexanoic and heptanoic acid, leading to the Kolbe-products R-R hydrocarbons, have been reported by J. D. WADHAWAN et al. 2001. The conversion of long chain carboxylic acids, i.e. fatty acids, and triglycerides via Non-Kolbe sonoelectrosynthesis has never before been reported. Applied sonochemistry, including sonoelectrosynthesis (oxidation and reduction), have been mainly developed on practical rather than theoretical basis, so that positive effects for different reactions have been reported, but some fundamental questions still remain unclear.

2.4 Electrofuels and Energetic Considerations

The intermittent nature of renewable energies, based on wind and solar power, calls for new technologies to convert the so far mainly unused electricity during overproduction into a storable form. As an example, there are current projects dealing with the conversion of energy into gaseous fuels like hydrogen or methane via electrolysis as reported by TRONCOSO and NEWBOROUGH 2011 and STERNBERG and BARDOW 2015, the so called power-to-fuel (e.g. power-to-gas and power-to-liquid) technology. The generated hydrogen can be used directly as fuel, chemical feedstock or converted to other fuel. The main limitation of this technology is the requirement of large storage volumes because of the low volumetric energy density of hydrogen, so that the generation of fuel with higher volumetric energy density present a clear advantage. The energy storage, by the production of biofuels has also been presented in a recent work from XIN et al. 2013, where electrocatalytic reduction of levulinic acid is employed. Recently RIDJAN et al. 2015 proposed a clear distinction of electrofuels from the term synthetic fuels in order to emphasize the benefit of producing fuel through this process, the term Electro-biorefinery XIN 2014 can also be found in this context. Figure 2.5 illustrates different fuel production processes of electrofuels, originally referring to electricity storage in form of liquid fuels through biological conversion of carbon dioxide or fuel production through carbon dioxide and hydrogen. In special cases when both carbon and electricity come from renewable sources, the derived fuel can be defined as renewable electrofuel.

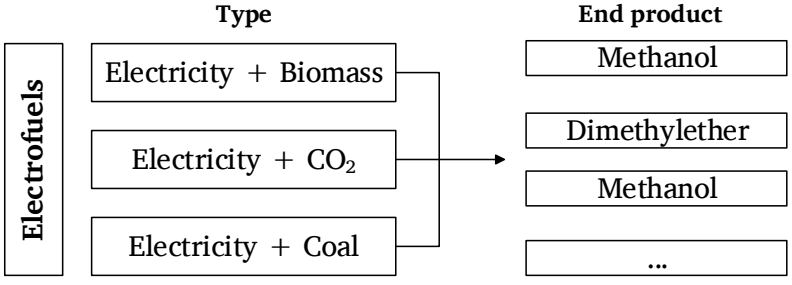

Figure 2.5: Electrofuel from different resources (adapted from RIDJAN et al. 2015)

In addition to the energy storage potential, the energetic consumption of the different reaction steps has to be assessed. A comparison of current petrochemical processes and the biomass conversion processes is only partly possible, since not all the different processes are in the same stage of development and optimization. Another important factor, that has to be taken into account, is the fact that some of the biomass derived products are still not available in large scale.

3 | Assessing the Suitability of Prospective Liquid Biofuels [1]

In this chapter some key properties, which can be experimentally determined in the chemical laboratory in test-tube quantities will be evaluated in order to allow a first assessment on the suitability of prospective biofuel molecules. This assessment is not to be understood as a comprehensive, since final information of a fuel is only available from test-engine runs, it is rather aimed to provide a strategy or guide for a practical evaluation of prospective biofuel options — a guide that shall also lead to a better understanding on how present biofuels can be improved and how future biofuels may be tailored. For simplicity and because in the present work pure substances are used, complex mixtures of petrol and biomass — often differing significantly from pure substances — are not in the focus of the following discussion. This also applies for combustion chemistry related challenges related to the application of (novel) biofuels, which are extensively discussed in (KOHSE-HÖINGHAUS et al. 2010). Noteworthy, the discussion is based on the respective DIN (Deutsches Institut für Normung, Berlin, Germany), EN ISO (International Organization for Standardization, Geneva, Switzerland) and ASTM (American Society for Testing and Materials, West Conshohocken, PA, USA) International standards, valid for Germany, Europe and USA, respectively. Therefore, the presented procedures and benchmarks may partially vary within other countries and regions of the world.

3.1 Origins and Properties of Prospective Biofuels

First of all, it should be noted that all processes that lead to a complete disintegration of the biomass (e.g. biomass gasification) and the subsequent use of the products in existing techniques (e.g. Fisher-Tropsch-syntheses) may sound advantageous, as they allow the exploitation of already established technological platforms (Figure 3.1). Thus, biofuels being

[1] This chapter has been published as Harnisch, F., Blei, I., **Santos, T. R. d.**, Möller, M., Nilges, P., Eilts, P., and Schröder, U. From the test-tube to the test-engine: assessing the suitability of prospective liquid biofuel compounds. RSC Adv., 3:9594-9605, 2013.

similar in their composition to current petro-chemical fuels, *e.g.* C_8-C_{20} alkanes for diesel fuel (MOLLENHAUER and TSCHÖKE 2007) can be gained. However, these processes are often based on high energy consumption and thus possess only a limited environmental benefit. Therefore, alternative (bio)chemical pathways, e.g. subcritical water processing of biomass (MÖLLER et al. 2011), may be advantageous from the energetic perspective. Yet, in general these processes yield a high diversity of molecules, possessing a broad variety of functionalities that may serve as seminal biofuels (Figure 3.1).

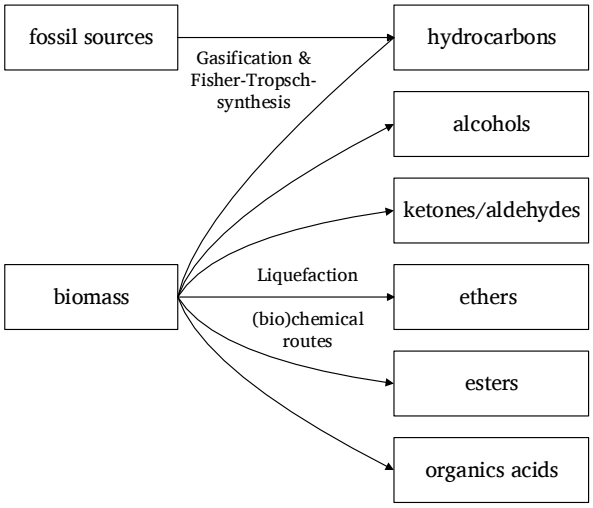

Figure 3.1: Major primary functionalities derived from fossil sources and biomass by gasification Fisher-Tropsch-syntheses and direct liquefaction as well as (bio)chemical transformation, respectively.

Using standard chemical separation and analytical methods the elemental composition of the mixture, the chemical structure of the molecules as well as their relative shares can be identified. However, this does not allow assessing the suitability of a pure compound to serve as automotive biofuel. Therefore, the determination of several key properties, allowing such assessment for even small quantities of a chemical compound to serve as a fuel for combustion engines, is desirable and necessary.

Table 3.1 summarizes a set of selected key parameters that may allow the rating of a biomass derived compound to serve as prospective biofuel. Certainly, the presented catalogue of properties might not be comprehensive — but may serve as a good basement. In order to illustrate these parameters, Table 3.2 summarizes typical values for petrochemical gasoline and diesel, biodiesel and (bio)ethanol.

Table 3.1: Key parameters of fuels and prospective biofuels - including a brief description, symbol, unit, respective legal definition (ISO, DIN, ASTM International) and laboratory-based determination method

Parameter	Brief description	Symbol	SI-Unit	DIN/ ISO	Laboratory based test method
		Fundamental properties			
Elemental composition	Elemental share of the respective elements C:H:O:N:S	ω	–	–	Elementary analyser
	Carbon Content	C	wt%	ASTM D3343	
	Hydrogen Content	H	wt%	ASTM D3343	
	Oxygen Content	O	wt%	EN 1601	
	Sulfur	S	wt%	EN ISO 20846	
	Nitrogen	N	wt%	ASTM D4629	
	Lead	Pb	wt%	EN 237	
	Phosphorous	p	wt%	ASTM D3231	
Density at 15°C	Mass per volume	ρ	$g\,cm^{-3}$	EN ISO 12185 EN ISO 3675 ASTM D4052	Aerometer, Pyknometer and others
Boiling point (for pure substances), boiling range (for mixtures) (at 1 bar)	Temperature of transition from liquid to gaseous phase	T_{Boil}	°C or K	EN ISO 3405	Distillery, boiling point apparatus
Melting/ freezing point (at 1 bar)	Temperature, where fuel becomes liquid/ solid	T_{Melt}	°C or K	ASTM D2386	Melting point apparatus
Viscosity/Rheological properties (at 40°C)	Describes fluidity of the fuel	μ or η	$mm^2\,s^{-1}$	EN ISO 3104	Viscosimeter, Rheometer
Calorific value (per mol)	Energy content per fuel molecule	ΔH_c^0	$J\,mol^{-1}$		Calorimeter
Calorific value (per mass) (Heat of Combustion)	Energy content per mass of fuel	ΔH_c^0	$J\,gfuel^{-1}$	ASTM D4809	Calorimeter
Calorific value (per volume)	Energy content per volume of fuel	ΔH_c^0	$J\,Lfuel^{-1}$		Calorimeter
Polarity / miscibility with standard liquid, here we propose heptane (vide infra)	Ability of the substances to form homogenous mixtures/ blends.		%		Miscibility test
Electric conductivity	Ability to conduct electric current	σ	$S\,m^{-1}$	DIN 51 412-2 ASTM D2624	Conductivity-meter
Water content	Content of mass H_2O per gram of fuel	u	wt%	EN ISO 12937	Karl-Fisher-titration
Strong acid number	Amount of KOH needed for neutralization per gram of fuel	TAN	mg_{KOH}/g	DIN 51 558 ASTM D664 DIN EN 15491	Acid-Base-Titration

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Table 3.1 – *Continued from previous page*

Parameter	Brief description	Symbol	SI-Unit	DIN/ ISO	Laboratory based test method
		Combustion engine related properties			
Cetane number	Measure of ease of ignition (diesel engine) ease of ignition of any fuel are compared to those of mixtures (CZ=100), iso-hexadecane (CZ=15) and 1-methylnaphtalin (CZ=0)	CN	–	EN ISO 5165 EN 15195 EN 16144 ASTM D 613	
Octane number motor octane number (MON) research octane number (RON) frontend octane number	Measure of anti-knock properties of motor fuel (gasoline engine) anti-knock properties of any fuel are compared to those of mixtures of n-heptane (RON=0) and isooctane (RON=100)	ON MON RON RON (100)	-	DIN ISO 5164 DIN ISO 5163	
Cold Filter Plugging Point (CFPP, summer)	Highest temperature, whre filtration through a standardizzed device fails	T_{CFPP}	°C or K	EN 116	Filter and cooling equipment
Ash content	Non-gaseous residue after burning the fuel	m_{Ash}	wt%	EN ISO 6245 ASTM D482	Residue after burning, balance
Autoignition temperture	Temperature, where fuel ignites without external ignition source	Θ_{AIT}	°C or K	DIN 51794	Several specialized devices, *e.g.* K47000
Oxidation stability	Resistance towards degradation process in air		$mg\,mL^{-1}$	DIN EN 590 EN ISO 12205 EN 15751	Specialized procedures, *e.g.* Rancimat method
Storage stability	(Experimentally extrapolated) stability for long-time storage (>1 year)		$g\,m^{-3}$	EN ISO 1220516	Fred Schäfer and Basshuysen 2004
Corrosivity	How much of a standard metal is lost after defined exposure to the fuel	$m_{weightloss}$ or class	mgmetal/gfuel/h or by visual classification	DIN 7120 (Stainless steel) EN ISO 2160 (Copper)	Specialized procedures, *e.g.* lab-corrosion test on copper or stainless steel
Reid vapour (at 37.8 °C)	Evaporation tendency at specified conditions	p_{VP}	bar	ASTM D 323	

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Table 3.1 – *Continued from previous page*

Parameter	Brief description	Symbol	SI-Unit	DIN/ ISO	Laboratory based test method
Health related properties					
Toxicity (dermal or oral)	Toxicity of the fuel is per kg of body weight, when swallowed or by skin contact (50% survival)	LD_{50}	$mg\,kg_{bodyweight}^{-1}$	–	Microbial toxicity test equipment
Toxicity (vapour or gas inhalation)	Toxicity of the fuel is per kg of body weight, when inhaled (50% survival)	LC_{50}	ppmV or $mg\,L^{-1}$	–	Microbial toxicity equipment
Mutagenic potential	Mutagenicity of the fuel in a specific test	–	pos./ neg.	DIN 38415-4 (Ames-test)	e.g. Ames-test, Microbial mutagenicity equipment

Table 3.2: Properties of selected established automotive petrochemical fuels and biofuels[a] (Ref. DIN 51625 2008; DIN 51628 2008; *DieselNet* 2010; F. Lackner et al. 2010; DIN 14214 2010; *National Toxicology Program - Departament of Health and Human Services* 2000; DIN EN ISO 7436 1996; *Shell Canada 1* 2010; *Shell Canada 2* 2010; *Thermo Fisher Scientific* 2015).

Parameter	Unit	Gasoline	Petro-diesel	Biodiesel (FAME)[b]1	Ethanol
Density (15°C)	$g\,cm^{-3}$	0.72-0.78	0.85-0.88	0.885 (0.882)	0.794
Melting point / Freezing point (at 1 bar)	°C or K	-40	-40 - 1	-3 – 18 (Cloud Point)	-114
Boiling point resp. boiling range (at 1 bar)	°C or K	27-225	180-340	299-346 (326-366)	78
Viscosity/Rheological properties (e.g. at 40°C)	$cSt(mm^2\,s^{-1})$	0.5-0.6	1.3-4.1	4.08 (4.83)	1.5
Calorific value (per mol)	$J\,mol^{-1}$	4.4	8.3	10.8	1.2
(calculated from the average molecular weight)					
Calorific value (per mass)	$MJ\,gfuel^{-1}$	43.4	42.8	37 (37.3)	27
Calorific value (per volume)	$MJ\,Lfuel^{-1}$	32.55	35.1	32.82	21.49
(calculated from the average density)					
Autoignition temperature	°C	257	315	177	423
Flash Point	°C	-43	60-80	131(170)	13
Toxicity (dermal)	$mg\,kg_{bodyweight}^{-1}$	>5	5000	2000	20
(oral)		>18	9000	>5000	6300
Toxicity (vapour	ppmV	300 ppm (TWA)	$1mg\,L^{-1}$	23-332 ppm	20000 ppm (10 h)
or gas inhalation)	$mg\,L^{-1}$	500 ppm(STEL)			
Mutagenic potential	pos./neg.	pos.	pos.	inconclusive	pos.
Ash content	wt%	–	0.01	–	–
Cold Filter Plugging point (CFPP, summer)	°C or K	n.a.	-10 –-10	-20–5	n.a.
Electric conductivity	$pS\,m^{-1}$	–	50	–	250
Corrosivity	Class	<1	1	1	1
Oxidation stability	h	6	20	6(110°C)	1
Reid Vapour pressure (at 37.8°C)	kPa	55–103	<1.5	<0.5	16
Water content	wt%	–	$200\,mg\,kg^{-1}$	$500mg\,kg^{-1}$	0.3
Neutralisation value (also strong acid number or strong base number)		<0.02	0.017	0.247	0.005

[a] n.a = not applicable; TWA=Time-weighted average; STEL=Short-term exposure

[b] Values refer to properties of soybean biodiesel with properties of rapeseebiodiesel in parentheses

One can clearly see that not all key parameter data are available for all types of fuel and may not even be applicable to novel (bio)fuels. This can be illustrated on the example of the calorific value: this is (surprisingly) not considered for standardized yet, as it is solely determined by the density for petrochemical fuels, thus in turn, the fuel density is considered as measure for standardization (this will be illustrated in section 3.2). Yet, from the presented data one can clearly deduce several obvious advantages and disadvantages of the respective fuel and its use in automotive combustion engines. For instance, when referring to the melting point or the CFPP respectively, it is evident that for temperatures around zero degrees Celsius some types of diesel fuel are not recommendable for regions with harsh winters, e.g. in Northern Europe, Northern America and Siberia.

However, in this context two major questions might be addressed, which may need a thorough discussion within the scientific community and that cannot comprehensively be answered within this work: 1) Do there exist knock-out criteria, i.e. properties that make a prospective fuel molecule inapplicable per se? 2) What are the limits of adjustment of a combustion engine towards a certain fuel, i.e. what are the lower and upper limit(s) of certain properties(s)?

For a first evaluation of a prospective biofuel, the following set of properties — derived from the petro-chemical diesel assessment (F. Lackner et al. 2010) — may serve as a fundament allowing a first assessment of a chemical substance: i) ignition properties: the cetane number(3.2), ii) calorific value (3.2), iii) greenhouse gas emission (3.2), iv) miscibility with a reference substance (3.2), v) viscosity and CFPP (3.2), vi) boiling range and volatility (3.2). Yet, this set of 6 core properties (discussed in 3.2 to 3.2) may only serve as a fundament and especially when referring to functionalized molecules (i.e. highly oxygen containing compounds) further properties have to be taken into consideration. Examples of some additional and also potentially decisive parameters are discussed in the last section (3.2).

3.2 Key-Properties of Diesel-like Biofuels and their Assessment

The properties listed in Table 3.1 can be classified as fundamental properties (*i.e* state variables) of the biofuel compound (or mixture) and engine related properties (*i.e* process parameters). Among the fundamental properties there are several that can be easily determined experimentally using standard chemical laboratory equipment. These include density, melting point (at 1 bar), boiling point (at 1 bar), viscosity, ash content and electric conductivity. Some of the fundamental properties and further properties need additional low-cost equipment and trained staff, e.g. water content and total acid number, which are both determined by titration (see DIN EN 15491 2007; DIN 51558 1979; ASTM 664 2011; EN ISO 12937 2002; ASTM E203 2008). Among these parameters may be further mutagenicity and toxicity as well as vapour pressure. For the latter, the Reid vapour pressure, i.e. the vapour pressure

at 100 °F = 37.8 °C is commonly used in combustion engine engineering. Yet, the determination of these parameters can be easily established in a (bio)chemical laboratory. For instance, for the calorific value a recalculation based on the thermodynamic values has to be performed (as shown in 3.2). Most of the engine related parameters (see Table 3.1 for examples), however, are often unusual for chemical laboratories and the ultimate suitability can only be assessed in a test engine (requiring large quantities). On the other hand, there are a number of semi-quantitative, engineering practices derived or data-base based methods (Table 3.3). These include, for instance the determination of the flash point according to SHIMY 1970, yet these approaches are limited to a certain range and class of chemical compounds. Furthermore, in physical chemistry there are concepts to derive thermo-physical properties based on the additivity rules (BENSON and BUSS 1958), with the Joback-method (JOBACK 1984) being the most prominent example. These methods have been improved stepwise by increasing the data-base fundament (ROWLEY et al. 2007) and expanded by non-linear regression functions, e.g. using neuronal networks (LAZZUS 2010) or quantum-mechanistic approaches (POLING et al. 2007). A clear advantage of these theoretical approaches is that the thermophysical properties of potential fuels can be assessed without the need of any substance. However, often these methods need (extensive) computational efforts and possesses a non-negligible error margin.

Therefore, in the following a catalogue of experimentally accessible properties requiring only test tube volumes of the prospective biofuel will be introduced. Thereby the assessment of the these properties in the (bio)chemical laboratory scale shall enable a first assessment of potential fuel molecules.

Table 3.3: Overview of the biofuel related properties and the respective theoretical assessment method, according to POLING et al. 2007

Property	Unit	Estimated using
Constant properties		
Melting point	K	JOBACK 1984
Boiling point	K	JOBACK 1984
Flash point	K	LAZZUS 2010; PAN et al. 2007
Flammability limits	Vol % in air	ALBAHRI 2003; HIRSCH and BRANDES 2005; SHIMY 1970
Auto ignition temperature	K	PAN et al. 2008; SHIMY 1970
Cetane number	–	DEFRIES et al. 2012
Heat of vaporization	$J\,mol^{-1}$	JOBACK 1984; PITZER 1995
Heat of formation	$J\,mol^{-1}$	BENSON and BUSS 1958; JOBACK 1984
Threshold sooting index (TSI)	–	PEPIOT-DESJARDINS et al. 2008
Heating value	$J\,mol^{-1}$	CAO et al. 2009
Temperature dependet properties		
Density	$mol\,m^{-3}$	RACKETT 2012; YAMADA and GUNN 2012
Liquid viscosity	$Pa\,s^{-1}$	JOBACK 1984
Heat of vaporization	$J\,mol^{-1}$	PITZER 1995
Ideal gas heat capacity	J mol K	BENSON and BUSS 1958; JOBACK 1984
Surface tension	$N\,m^{-1}$	PITZER 1995
Vapor pressure of liquid	Pa	PITZER 1995

Ignition Properties: the Cetane Number

The cetane number (CN) is a well estabilshed parameter to characterize diesel fuels on their ignition quality or ignition delay (F. Lackner et al. 2010). However, the combustion does strongly depend on the (typ of) engine, it operation enviroment an the fuel itself. Furthermore, the CN scale and benchmarks are originating from the petro-diesel era an are thus not perfectly suitable for biofuel characterization (Groth and Hesse 1985), especially for alternative combustion systems. Yet, for convinience the CN may serve as a starting point for forthcoming adjustments in te technological sector.

It is well known that the chemical structure has a severe impact on the CN of a fuel, and as a rule of thumb it can be stated taht CN decreases as follws: n-alkanes > alkenes > cycloalkanes > aromates (Pischinger et al. 2002; Song et al. 2000). Typical petro-diesel possesses a CN of 40 to 55, for the EU > 51 (DIN EN 590 2010). However, the exact determination of the cetane number is not trivial. Generally the CN is determined using certified, specialized engines (ASTM D613 2014), *e.g.* the BASF-engine or the Cooperative Fuel Research-engine (CFR-engine), that require several litres of the fuel. A recent alternative is the assessment using an ignition quality tester (IQT) (ASTM D6890 2013; IP 498 2008; EN 15195 2005), which is a device that needs only hundred milliliters (Stanhope-Seta 2012) of a fuel and provides a good approximation of its ignition quality. It has recently been shown that, especially for novel fuels possessing oxygen moieties, the IQT is better suited than the CFR- or BASF-engine (Attenberger and Remmele 2005), for instance, due to differences in the fuel injeaction system and the combustion chamber (Gary et al. 2007).

Interestingly, the CFR-engine was introduced (and standardized) in 1936 and did not change so far (ASTM D613 2014), as a consequence such a test is not comparable to a state-of-the art diesel engine of modern vehicles and its combustion properties (N. Elliott 2009). This is only slightly different for the BASF-engine. As not every refinery has access to test engines, also the matematical assessment of the combustion properties of petro-chemicals is applied. Here the so called cetane index (CI), an alternative classification that is related to the CN for petro-diesel, is calculated from fuel volatility and density of a respective sample (Azev et al. 1978; ASTM D4737-10 1998). However, as these methods can only be applied for petro-diesel with CN higher than 40 (Azev et al. 1978; ASTM D4737-10 1998; ASTM D976-06 2011) they can be considered to be truly in their infancy in regard to the assessment of alternative biofuels.

As alternative option — that can be realized in the chemical laboratory but is not based on any engine related properties — an assessment of the ignition quality based on the auto-ignition temperature (AIT), Θ_{AIT}, of the fuel is proposed; following a proposal more than 20 years for petro-chemicals fuels (Groth and Hesse 1985; ASTM D4737-10 1998; ASTM D976-06 2011). The auto-ignition temperature, Θ_{AIT}, is the temperature, at which a substance spontaneously ignites in the ambient atmosphere without an external ignition source. In

principle Θ_{AIT} can be determinated with very samll experimental effort (DIN 1794 2003; ASTM E659 2014); and nowdays standard laboratory equipment is avaiable at reasonable costs. Noteworthy, Θ_{AIT}, should not be confused with the flash point, denominating the temperature, where ignition by and external source takes place. Thus the later is of special interest for safety issues. Figure 3.2 shows the cetane numbers, determined using test engine runs, as function of the auto-ignition temperature of the respective substance (see A.1). As one can clearly see there is a clear trend for a decrease of the cetane numbers, determined using test engine runs, as a function of the auto-ignition temperature. This decrease is independent of the functional groups of a given substance. For instance 2,4-dimethylpentane and 3-octanone are clearly different chemical substances, but possess an close auto-ignition temperature (of 337 °C and 330 °C, respectivily) and cetane number (DIN 51625 2008; *Shell Canada 1* 2010 respectively). Therefore, the auto-ignition temperature can be suggested of being a valuable initial measure in order to assess the suitability of a prospective biofuel substance. However, especially for substances possessing a medium range Θ_{AIT} the prediction of the CN seems only of limited value and only for very high or very low Θ_{AIT} the prediction seems straightforward.

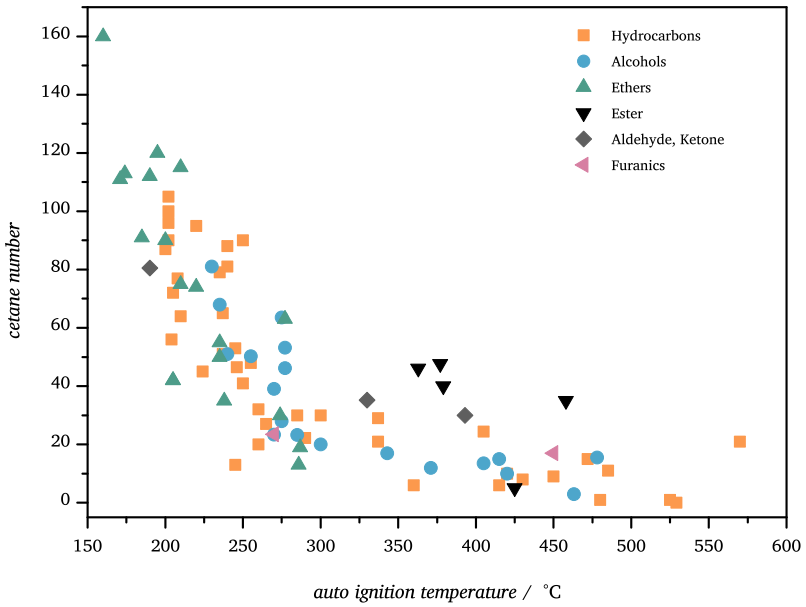

Figure 3.2: Cetane number (CN) as function of the auto-ignition temperature for different substances, clustered according to their functional groups as indicated (see A.1 for the raw data and references)

In this context it is worth to mention that numerous efforts have been made to theoretically calculate these properties (CN, CI and AIT) from molecular composition of crude oil fractions (Egolf and Jurs 1992). Yet, it might be questionable if these almost exclusively phenomenological procedures can be expanded to non-petrochemical compounds. Infor-

mation on the fuel combustion might be derived from other data source, *e.g.* dealing with fire-and explosion-protection (GÖDDE et al. 1998) or the molecular building enthalpies of the respective compounds. The latter heat of formation values, H_f, shows a clear substance specific behavior (Figure 3.3). Figure 3.3 shows a clear sequence of the substance classes and dependencies within a given class of substance, within exception of the ethers; for furans and aldehydes/ketones only limited data was available. Furthermore it has to be taken into consideration that fuel additives, chemical substances in small amounts, can be used to tailor the combustion behavior significantly (DIN EN 15491 2007; DIN 51558 1979; ASTM 664 2011; EN ISO 12937 2002; ASTM E203 2008).

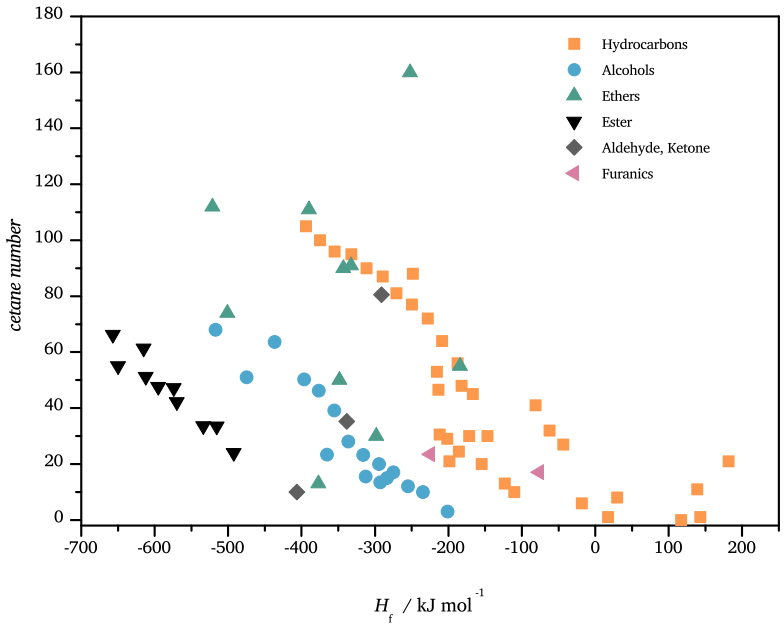

Figure 3.3: Cetane number as function of the heat of formation for different substances, clustered according to their funtional groups (see A.1 for the raw data and references)

Calorific Value

The energy content of a fuel is certainly one of the most important and most straightforward criterion for judging a potential biofuel, as it determines how much energy can be exploited for motion. From the purely thermodynamic point of view the caloric value, *i.e.* heat of combustion, of a chemical compound or mixture is univocal and can be calculated (ASTM D1405/D1405M 2008; ASTM D3338/D3338M-08 2014) or can be experimentally measured using a bomb calorimeter (D.R STULL and C.SINKE 1969). In this regard, the heat of combustion can be normalized per molecule – that is often most suitable for chemical calculations, but not applicable to complex fuel mixtures like petro-diesel. Here, the energy content per mass or volume (both can be easily accessed in the chemical laboratory) of the fuel are often

more relevant from the engineering perspective in order to minimize the automobiles tank volumes and weights.

The mass related calorific value of a fuel (determined in a calorimeter while facing an oxygen atmosphere) is also denominated as the higher heating value, H_{HHV} (ASTM D240 2014; DIN 51900-1 2000). For H_{HHV} the heat of condensation (of water) is considered, but it is not when the lower heating value, H_{LHV}, is reported. As after combustion in an engine water appears as vapour the H_{LHV}has to be considered for all further discussions. Considering a complete combustion of chemical compounds (or mixtures thereof) the respective heat of combustion is calculated from their elemental composition, using phenomenological equations deriving from petro-chemical combustion engineering (Brandt 1999). In the following the widely used methods of Dulong and Boie (Boie 1957) shall be used to illustrate the procedure (Beiz and Grot 2011) (with the symbols representing the relative mass shares, ω, of the elements and water).

Method according to Dulong (Grote and Feldhusen 2005):

$$H_{\mathrm{LHV}} = 33.9\omega_{\mathrm{C}} + 121.4(\omega_{\mathrm{H}} - \omega_{\mathrm{O}}/8) + 10.5\omega_{\mathrm{S}} - 2.44\omega_{\mathrm{H2O}} \tag{3.1}$$

Method according to Boie (Grote and Feldhusen 2005):

$$H_{\mathrm{LHV}} = 34.8\omega_{\mathrm{C}} + 93.9\omega_{\mathrm{H}} - 10.8\omega_{\mathrm{O}} + 10.5\omega_{\mathrm{S}} + 6.3\omega_{\mathrm{N}} - 2.44\omega_{\mathrm{H2O}} \tag{3.2}$$

Thus, when considering a molecule $C_xH_yO_z$, obviously the highest H_{LHV} can be gained for pure H_2 (x=0 and y=2) and lowest for pure carbon (x=1 and y=0); H_{LHV} = 121 kJ g^{-1} and H_{LHV} = 32.8 kJ g^{-1} respectively. When considering H_2 the formula according to Dulong yields 121.4 kJ g^{-1}, whereas the calculation to Boie deviates about 20 %. When considering alternative fuels, possessing the composition CxHyOz, H_{LHV} decreases with increasing oxygen content. Therefore, when considering potential biofuels, the oxygen content of the molecule plays a key role. However, only limited experimental calorific data for the assessment of propectives biofuel candidates is available.

Figure 3.4 shows an exemplary calculation of the H_{LHV} using the different methods introduced above as function of the experimentally assessed lower heating value (see A.1 for raw data). One can clearly see that the method according to Dulong overestimates the H_{LHV}, especially for compounds with a higher calorific value, whereas the method using the Boie algorithm seems to result in a better fitting. However, both algorithms still differ from the experimental value. These deviations are of special interest, as the H_{LHV} usually serves as input parameter for the adjustment of the engine to the fuels as well as the calculation of the fuel consumption of a given engine. Interestingly, the H_{LHV} is not included in the respective norms/standards regulation the fuel market (DIN EN 590 2010). Here only the boiling behavior and the density of a fuel have to be reported, as both are decisive for the volu-

metrically standardized fuel refill at the station. As a consequence the volumetric heat of combustion of diesel is usually 10 % higher (due to its higher density) in comparison to gasoline, though the weight related heats of combustion are similar (MOLLENHAUER and TSCHÖKE 2007). From the combustion engine engineer's perspective the calorific value of

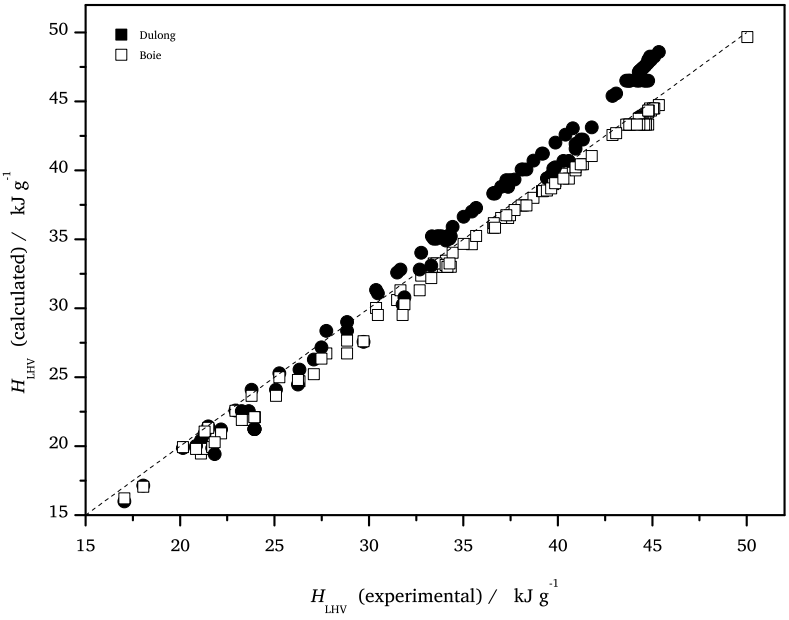

Figure 3.4: Comparison of the experimental lower heating value in comparison to the theoretical values determined by the method of Boie and Dulong (see A.1 for the raw data and references)

the fuel/air-mixture, H_{mix}, is the key parameter as it determines the engine's power output (DIN EN 15751 2009). Thus the combustion stoichiometry, assuming a complete oxidation of fuel, is decisive. Here the air needed for a complete combustion is called stoichiometric air requirement, L_{St}, and can be calculated from the C:H:0:S ratio as follows (PISCHINGER et al. 2002):

$$L_{\mathrm{St}} = 137.8(\omega_{\mathrm{C}}/12.01 + \omega_{\mathrm{H}}/4.031 + \omega_{\mathrm{S}}/32.06 - \omega_{\mathrm{O}}/32.00) \tag{3.3}$$

Figure 3.5 shows the H_{LHV} of different classes of substances as function of the stoichiometrically air (21 % of O_2) requirement L_{St}. As H_{mix} is not solely a function of the caloric value of the fuel, but also of the fuel/air ration needed for combustion, it can be calculated as shown in 3.4 (for air induction diesel engines):

$$H_{\mathrm{mix}} = H_{\mathrm{LHV}}\rho_L / \lambda L_{St} \tag{3.4}$$

(H_{mix} and H_{LHV} being the calorific value of the combustible air-fuel mixture and the lower heating value of the fuel respectively; ρ_L being the density of air and λ being the excess air factor)

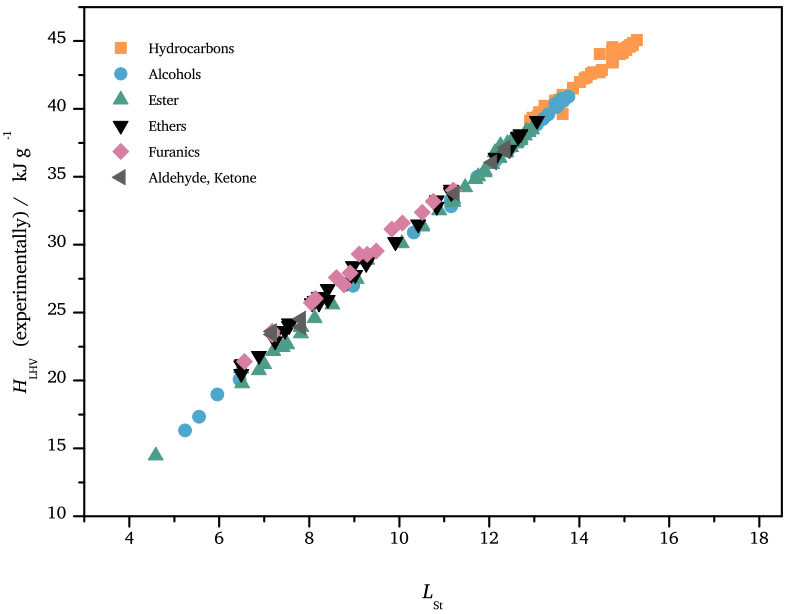

Figure 3.5: Lower heating value (experimental) as function of the stoichiometric air requirement for different classes of chemical substances (see A.1 for the raw data and references)

Figure 3.6 shows the H_{mix} as function of L_{St} for different substances as well as four reference fuels. One can clearly see that the studied hydrocarbons and alcohols cluster and show a linear dependence on the number of C-molecules, with exception of methanol and the dio ethylen-glycol and triol glycerol for the latter. Most other substances of all other substance classes, however, show a more scattered pattern. In pratical terms, however, H_{mix} is strongly dependent on the actual air requirement of the engine (PISCHINGER et al. 2002).

Estimation of Greenhouse Gas Emission

During the combustion processes several greenhouse gases are emitted. Whereas some emissions (e.g. NOx) can be avoided by proper adjustment of the combustion engine, carbon dioxide emission cannot be avoided during fuel combustion. In principle, the emitted carbon dioxide per fuel molecule can be easily calculated from the elemental composition. Here, the CO_2-emision should be related to the respective heat of combustion of the molecule, as it is the aim to decrease the formation of greenhouse gas per utilized energy. The respective CO_2 emission can be calculated (considering optimal combustion) from the reaction stoichiometry. Based thereon, the specificCO_2 emission of a fuel as function of the H_{LHV} can be calculated. This value may serve as a measure to characterize a fuel in terms of its greenhouse gas emission impact. In Figure 3.7 this coefficient is plotted as function of the specific C:H ratio of a given fuel. This plot shows an interesting behavior, as it clearly

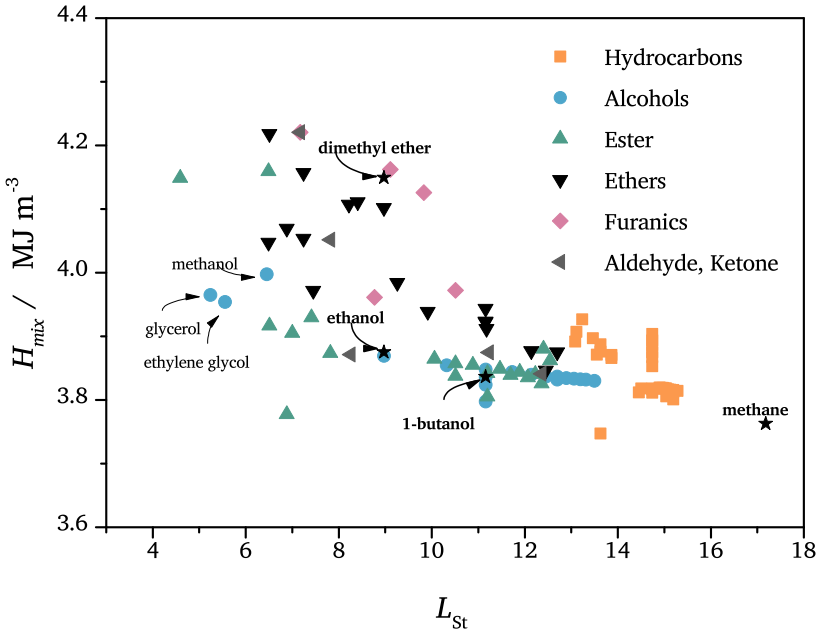

Figure 3.6: Calorific value of the fue/air mixture (experimental) as function of the stoichiometric air requirement for different classes of chemical substances and selected reference fuels ($\lambda = 1$) (see A.1 for the raw data and references)

demonstrates that within the class of hydrocarbons a longer chain length and higher degree of aromaticity increase the carbon dioxide formation per mega-joule. For other compounds a more scattered picture is observed and only very few compounds possess a lower greenhouse gas emission behavior than standard petro-diesel. However, this analysis does not account for the emissions during fuel production, here a more thorough analysis of "well to wheel" has to be performed (HÖHLEIN et al. 2010).

Furthermore, the non-ideal combustion in an engine that leads to further emissions has to be considered, including for instance soot formation, as function of the C:H-ratio, as well as the ignition delay (resulting *e.g.* in an increased pressure rise and thus noise emission). However, these parameters are not specific for a prospective biofuel a priori, but are related to the fuel-engine system and have to be assessed and tailored in the further biofuel development.

Miscibility with a Reference

In the majority of cases automotive fuels are not pure substances, but blends, *i.e.* a mixture of different chemical compounds. In case of petro-diesel often not all constituintes are even know. A novel (bioderived) fuel constituents are applied not as pure compounds, but as blends, e.g. diesel with 7 % of FAME (denominated as *B7* in Europe (DIN EN 590 2010)), the

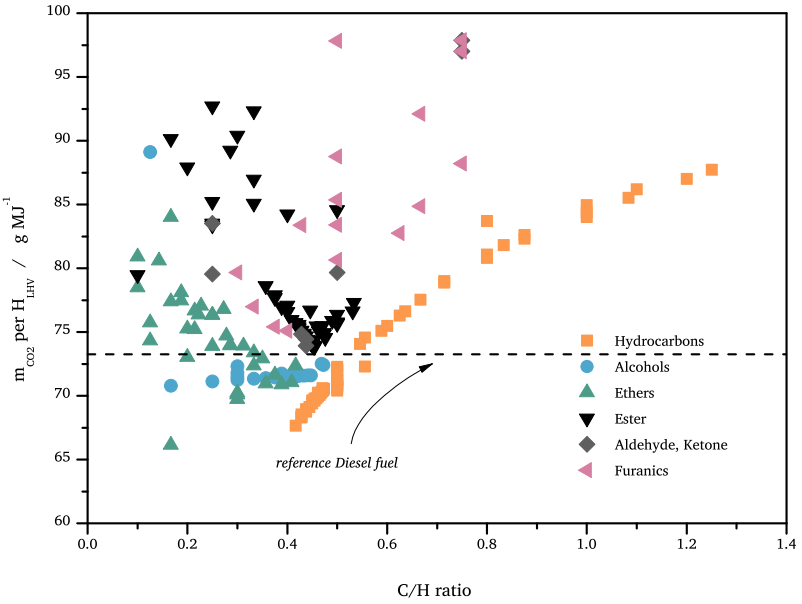

Figure 3.7: CO_2-emission per MJ of heat of combustion as function of the C:H-ratio of different classes of potential biofuel molecules (see A.1 for the raw data and references)

miscibility of the novel biofuel molecule with the existing standard fuel is a key prerequisite for its introduction into the market. However, from the chemist's perspective petro-diesel is a complex mixture with high variety and variability of its molecular constituintes. Therefore, an alternative could be to report the miscibility of every prospective (potentially diesel substituing) biofuel molecule with a primary reference fuel (PRF). Here a pure chemical compound like n-hepatane, a C_7-unbranched and not functionalized alkane, can be assumed as a potential model compound for petrochemical diesel-fuels (Baumgarten 2006; Curran et al. 1998; Müller 1993) or a mixture with iso-octane (in accordance with Janssen et al. 2012), cetane, iso-hexadecane and 1-methylnaphtaline or a petrochemical reference diesel can be used. In addition it might be useful to determine some of the discussed criteria for the respective pure compounds as well as for specified mixtures of the compound and the standard.

Viscosity and Cold filter Plugging Point

The viscosity of a fuel is highly relevante for its transfer from the fuel tank to the engine's combustion chamber. Especially at low temperatures, *i.e.* in colder climates or during the engine starting-phase, a malfunction of the fuels spray formation can lead to an inhomogeneous formation of the fuel/air-mixture and thus increased fuel consumption and high emissions. This can be adjusted, to a certain extent, by tailoring the combustion engine to-

wards the respective fuel. For instance, this is done for marine engines, where a pre-heating of the fuel reservoir is installed, (FRED SCHÄFER and BASSHUYSEN 2004) yet this might not be applicable for automotive usage. Closely related to the viscosity and melting point is the Cold Filter Plugging Point (CFPP) of a fuel. The CFPP is defined as the highest temperature at which a certain volume of the fuel, cooled down using a prescribed regime, cannot be pressed through a standardized filter (JANSSEN et al. 2012). This test might be performed in a chemical laboratory; however, a specialized, acquired or self-made device is needed, see (DIN EN 116 2009) for experimental details. Here also the fuel's lubricity, a complex and, so far, hard to predict or calculate property has to be considereded (KNOTHE and STEIDLEY 2005). This parameter can be determined in the laboratory in volumes as low as 2 ml (EN ISO 12156-1:2006 2008).

Boiling Point and Volatility

The boiling characteristics of a fuel can be decisive for the engine's performance, especially the oil dilution and thus for the overall performance. Whereas pure substances posses a boiling point, complex mixtures (like most fuels) boil over a wide temperature range. This is illustrated in Figure 3.8 showing the boiling point of n-hexadecane (cetane) and some exemplary petro-diesels. This clearly illustrates the wide temperature range of established fuels and thus the potential wide window from 150 °C to 350 °C of novel biofuel compounds. In this context, several characteristics points, T_{10}, T_{50} and T_{90}, denominate the respective

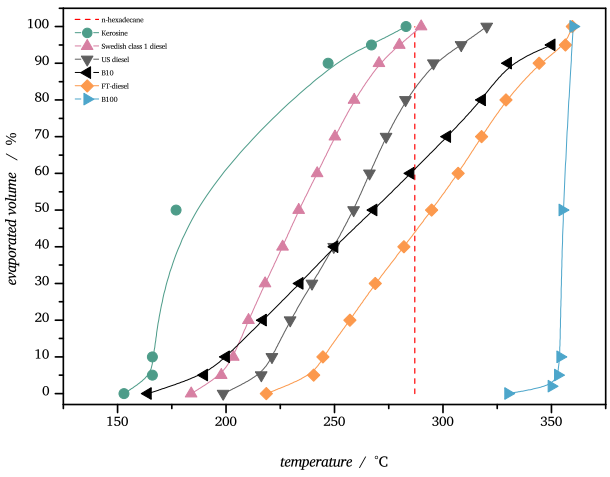

Figure 3.8: Boiling curves of selected petro-diesels and boiling point of n-hexadecane (defining a cetane number of 100) (see Table A.7 and Table A.8 for data and references)

temperature for 10 %, 50 % or 90 % of a fuel mixture being in the gas phase. For diesel like fuels, it can be stated (assuming today's engines of the automotive fleet) that the boiling T_{95} should not exceed to high temperatures, *e.g.* 360 °C (EN ISO 3405 2011). Compounds

boiling at higher temperatures possess several negatives effects, for instance they may lead to increase CO_2- emissions, sooting (*i.e.* carburization during the burning process) and oil dilution (DEMIRBAS 2007). Therefore, new biodiesel compounds (at least for current engine technology) should possess no higher boiling temperature than 360 °C. Furthermore, the boiling point of a substance, or the beginning of a boiling curve of a fuel mixture, is a strong indicator for its volatility (see also storage stability). Finally, it has to be noted that the lab based assessment of the boiling temperature can not substitute the test engine runs, as only the latter can provide ultimate data for biofuel properties under real application conditions. Yet, the above described assessments can provide significant information, if a substance (pure or blended) is worth to be considered as a fuel.

Determination of Further Selected Properties

Oxidation/Storage Stability: Not only evaporation - as discussed in 3.2 - may lead to a loss of fuel, but also chemical transformation, generally oxidation, may cause a limited storage stability of the fuel, also including safety hazards due to possible peroxide formation. Therefore, the stability of the molecule in the presence of air and/or moisture has to be evaluated. This is of high importance for the long time storage stability of the fuel. Therefore, oxidation and polymerization processes, causing the limited stability of the fuel, have to be simulated experimentally in the laboratory. In this context, different set-ups, especially for the comparison of petro-diesel and biodiesel, have been proposed. (DEMIRBAS 2007; MUNACK et al. 2009) In all these procedures, the fuel is heated in a moisture and/or oxygen containing atmosphere for a defined time, in order to evaluate the reaction rates of the polymerization and oxidation reactions. One method taht might serve as a standard is the DIN ISO 12205, here the fuel is heated to 95 °C in a open vessel for 16 h in a oxygen atmosphere (3 l O_2 h^{-1}) (DIN EN ISO 12205 1996). As O_2 - atmospheres are not applicable in every laboratory, air might replace the oxygen in the set-up. However, this has to be clearly indicated as well as further variations in the conditions, which might often occur due to "in-house" standards. As an indicator of stability the formation of insoluble compounds, often denominated as "insoluble resins", should be reported, *e.g.* in g m^{-3}fuel. Noteworthy, these insoluble compounds comprise the filter residue, when filtering the fuel after the above described aging simulation, as well as the residues adhering to the vessel.

Corrosivity: Obviously, the fuel should not harm the engine and all other parts it is in contact with. Yet, during transportation and storage fuels have contact to various metals, and are exposed to oxygen and moisture. The products formed may lead to corrosion on different parts of the engine and fuel piping system. In order to assess a fuel prospective corrosivity, its corrosion effect on stainless steel and copper using standardizes procedures is generally reported. According to DIN ISO 7120 2007 a stainless steel rod is exposed to a mixture of fuel and distilled water (ratio 10 : 1) at 60 °C for 24 hour. After finishing the test, the corrosion effect is assessed by visual inspection and classification; alternatively (and more common to

chemical researchers) the corrosion rate in mass per time EN ISO 2160 1995 can be reported. Furthermore, here the reactivity of the biofuel with plastic materials, *e.g.* seals, has to be considered.

Density: The density of a fuel is the mass per unit volume of fuel at a given temperature that can easily be measured in the laboratory. Obviously, this has a direct impact on the volumetric energy content (3.2). This is of special interest for current combustion engines, as the dimensions of the components of the injection system is based on the fuel volume and thus a change in the fuel density an thus in the volumetric energy content would need its replacement/readjustment in order to obtain an optimum fuel conversion by the engine. As discussed, an improper engine operation will not only limit the power output, but also lead to an increased formation of soot and other pollutants.

4 | Methods and Procedures

This chapter is divided into two sections 4.1 and 4.2 and should aside from describing the experimental procedures also briefly explain some details about the chosen methods.

4.1 Chemical Analytical Approach

The analysis of the starting materials and resulting products from electroorganic syntheses plays an important role for the evaluation of reaction performance. Although the aimed products achieved via electrochemical conversion should mostly be compatible with petrochemical derived compounds, current analytical protocols were not always ideally suited for the analyses in some more specific reaction conditions. High salt contents and reactions in aqueous environmental were two issues to be addressed in this context. Therefore, tailored and more specific protocols like (both quantitatively and qualitative) concerning the respective target molecules were established. Figure 4.1 illustrates the chemical analytical concept proposed in the current work, based on the specific existing laboratory infrastructure.

As Figure 4.1 shows, a complete analysis involves the measurement of liquid phase (both aqueous and organic) and gas phase, since the target compounds were mainly found in the liquid phase, the gas phase was measured only exemplary for selected samples. The methods employed are known analytical techniques, so this chapter will only give an overview on the steps applied in each particular case. The next paragraphs present details to be considered for both reaction pathway studied in this work: levulinic acid and fatty acids. In Section 4.1.1 the experimental conditions for the applied analysis methods are described.

Levulinic acid reaction pathway (analysis of short-chain (C$\leq$8) compounds:) Both, educts and products derived from the levulinic acid reaction pathway are in the present work called short-chain compounds, having at the maximum 8 carbons. If the reaction took place in an aqueous medium and all products formed are water soluble at the applied concentration, high-performance liquid chromatography (HPLC) was used as a routine tool for the analysis

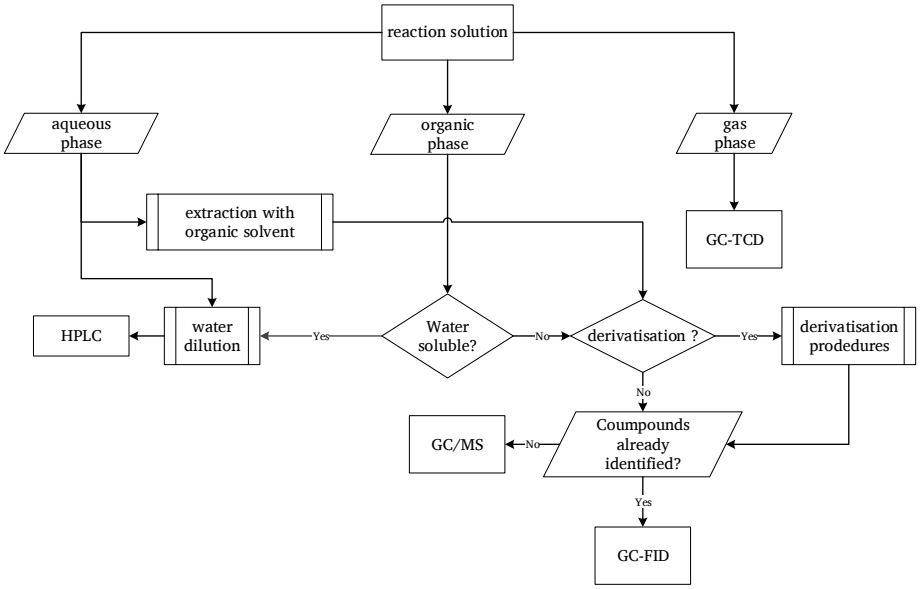

Figure 4.1: Schematic illustration for the chemical analytic methods

of short chain carboxylic acids and water soluble derived compounds (for details see Section 4.1.1.1). Before HPLC analysis samples were the acidified to pH 1 with diluted H_2SO_4 and diluted according to the calibration range.

Some reactions pathways lead to the formation of water insoluble compounds. If the phase separation was only a matter of saturation of the aqueous phase, the reaction solution was diluted with water after electrolysis was finished. If the organic phase was water insoluble, this phase was separated and diluted in an organic solvent for further analysis with GC.

Analysis of Long-chain Fatty Acids without Derivatization: The simultaneous analysis of long-chain fatty acids and hydrocarbons is not a trivial task and the establishment of a suitable analysis protocol was the first step necessary for the evaluation of the electrochemical reactions for the long fatty acids pathway (Chapter 6). Carboxylic acids posses significantly higher boiling points than the corresponding alkanes, alkenes and esters, which represents a problem especially for standard GC analyzes. Separating carboxylated compounds by GC is complicated by their relatively high polarity and therefore derivatization prior to analysis is commonly needed (Hallmann et al. 2008). The derivatization, specially the methylation, of the fatty acids is according to the literature often the better solution to perform this analysis and it is currently the standard method (DIN EN 14103 2009). However, optimum derivatization varies strongly for different acids and no single derivatization protocol can be employed without certain losses (Hallmann et al. 2008).

A part from avoiding further sample preparation steps after the reaction and possible sources of errors, the formation of methyl and ethyl esters as by-products by the electrochemical con-

version in organic solvent (see Figure 6.1) was a decisive factor for considering an alternative protocol for the analysis of long chain fatty acids. HALLMANN et al. 2008 describes the butylation of carboxylic acid as an attractive alternative to methylation. The main limitation of this method is the considerable error in quantitative analysis of individual types of carboxylic acid. Considering the need of a flexible protocol a method without derivatization was preferred. Therefore a method using a column with higher polarity was chosen. The chemically-bonded free fatty acid phase (FFAP) capillary column provides good qualitative resolution of underivatized fatty acids with up to twenty carbon atoms (CHENG and LI 2005). The main limitation of the nonderivatization is due to sample losses in the GC system and for this reason the analysis of free fatty acids cannot be performed reliably when dealing with minor amount of sample (VIČANOVÁ et al. 1994. The described method for the determination of underivatized fatty acids is simple and relative fast. Good linearity was observed for all over the standard curve concentration range of 10 ng μL^{-1} to 250 ng μL^{-1}.

Although FFAP columns tolerate aqueous samples, the influence of dissolved salts is a limitation for the direct injection of salt-containing aqueous samples. Therefore supporting electrolyte and water has to be removed in order to avoid contaminating the inlet causing adsorption and response loss over the time. For this purpose, the following procedure was used: The salt containing sample was acidified to pH 1 with diluted H_2SO_4 and the organic compounds were extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution in order to improve the phase separation and the organic extracts were dried over magnesium sulfate ($MgSO_4$). The ethyl acetate phase was filtered using a syringe filter (Phenex-RC 15 mm, 0.2 µm, Non-Sterile) and diluted according to the calibration range (see section 4.1.1.2).

Even though this protocol was successfully applied for the analysis of free fatty acids, it is not directly suitable for the analysis of triglycerides as rapeseed oil especially due to the higher boiling point of triglycerides. There are many different methods described in literature for the analysis of triglycerides, particularly relevant are the chromatographic methods combined with spectroscopic techniques. Within the scope of this work neither a complex lipid characterization nor an intact triglyceride profiling was necessary, since the predetermined target compounds and their concentrations were the aim of the analysis. For this purpose, as discussed before, triglycerides are as usually converted into fatty acid methyl esters for gas chromatography analysis. Particularly in view of the fact that direct electrochemical conversion of triglycerides was only possible in aqueous medium, the methylation did not disturb the evaluation of these specific reactions. Since the emulsion was stable during and after the experiments, an emulsion breaking using concentrated sulfuric acid was necessary prior to further quantitative analysis as described below (see Section 4.1.1.2). This emulsion breaking method could also be an alternative for the separation step after reaction in larger scale.

4.1.1 Analysis Methods

After some preliminary experiments, the following methods were applied for the different reactions pathways according to the schema presented in Figure 4.1:

4.1.1.1 High-performance liquid chromatography (HPLC)

Levulinic acid and reactions products: Routine substance quantification in the aqueous phase was obtained by a HPLC system (Spectrasystem P4000, Finnigan Surveyor RI Plus Detector, Fisher Scientific) equipped with a HyperREZ XP Carbohydrate H+ 8 µm (S/N: 026/H/012-227). Sulfuric acid (0.005 N, flow rate 0.5 mL min^{-1}) served as the eluent. The column was operated at different temperature depending on sample composition; the refractory index detector was operated at 40 °C.

Quantitative analysis was further realized with a HPLC-UV/VIS system (Hewlett Packard Series 1050, Hewlett Packard, United States of America) with a DAD-detector and equipped with a HyperREZ XP Carbohydrate H+ 8 µm (S/N: 026/H/012-227). Phosphoric acid (0.05 %, flow rate 0.5 mL min^{-1}) served as the eluent. The column was kept at room temperature. Educt and product concentrations were determined by both HPLC systems using calibration curves in a range from 0 M to 0.2 M.

Glycerol: A HPLC system (Spectrasystem P4000, Finnigan Surveyor RI Plus Detector, Fisher Scientific) equipped with a HyperREZ XP Carbohydrate H+ 8 µm (S/N: 026/H/012-227) column was used for routine substance quantification (in the aqueous phase). Sulfuric acid (0.005 N, flow rate 0.5 mL min^{-1}) served as the eluent. The column was kept at room temperature; the refractory index detector was set at 40 °C during measurements. Glycerol concentrations were determined using external calibration curves in a range from 0 M to 0.1 M.

4.1.1.2 Gas chromatography-flame Ionization detector (GC-FID)

Long chain fatty acid and reaction products: Quantitative and qualitative analyses of free fatty acids and the respective reaction products were carried out without further derivatization by GC-FID (Hewlett Packard Series II 5890) equipped with a DB-FFAP (30 m x 0.25 mm ID x 0.25 µm film, GC column from Agilent JW Scientific, USA). External calibration curves with different concentration levels in a range from 0 ng μL^{-1} to 250 ng μL^{-1} were used for the quantification. Injector: Split/Splitless. Injector temperature.: 250 °C, Detector 250 °C, Splitless injection, const. flow mode: 2.00 mL min^{-1}, 100 °C for 10 min with rate of 10 °C min^{-1} to 250 °C and hold for 20 min.

4.1.1.3 Gas chromatography–mass spectrometry (GC-MS)

Levulinic acid and reactions products: Qualitative analysis was carried out using GC-MS (Trace GC Ultra, DSQ II, Thermo Scientific, Germany) equipped with a TR-Wax MS (30 m x 0.25 mm ID x 0.25 µm film GC column, Thermo Scientific, Germany). Ionensource: 220 °C, Injector: Split/Splitless. Injectortemp: 260 °C, Splitflow: 50 mL min^{-1}, Splitlesstime: 1 min. const. flow mode: 1.00 mL min^{-1}, transferline: 335 °C, oven: 40 °C to 150 °C with rate of 10 °C min^{-1} and hold for 1 min.

Long chain fatty acid and reaction products: Qualitative and quantitative analyses were carried out using GC-MS (Trace GC Ultra, DSQ II, Thermo Scientific, Germany) equipped with a TR-5MS (30 m x 0.25 mm ID x 0.25 µm film GC column Thermo Scientific, Germany) or TR-Wax MS (30 m x 0.25 mm ID x 0.25 µm film GC column, Thermo Scientific, Germany). Ionensource: 220 °C, Injector: Split/Splitless. Injectortemp: 260 °C, Splitflow: 50 mL min^{-1}, Splitlesstime: 1 min. const. flow mode: 1.00 mL min^{-1}, transferline: 335 °C, oven: 40 °C for 4 min with rate of 20 °C min^{-1} to 330 °C and hold for 10 min.

Figure 4.2 illustrates exemplary the product mixture of the decarboxylation of different fatty acids in methanol or ethanol and Table 4.1 shows the respective retention time of the main detected products.

Table 4.1: Summary of the main products detected by GC/MS

		Palmitic acid		Stearic acid		Oleic acid	
		compound	RT	compound	RT	compound	RT
olefine		1-pentadecene	16.20	1-heptadecene	18.56	(Z)-hetapdece-8-ene	18.79
						(E)-hetapdece-8-ene	
						(Z)-hetapdeca-1,8-diene	18.31
						(Z)-hetapdeca-1,8-diene	
ether	ethanol	1-ethoxy- pentadecane	18.87	1-ethoxy- heptadecane	20.95	(Z)-17-ethoxy-heptadec-8-ene	20.69
						(E)-17-ethoxyheptadec-8-ene	
	methanol	1-methoxy- pentadecane	18.40	1-methoxy- heptadecane	20.54	(Z)-17-methoxy-heptadec-8-ene	20.30
						(E)-17-methoxyheptadec-8-ene	
by-prodcut	ethanol	ethylpalmitate	19.59	ethyl stearate	20.95	ethyl oleate	21.37
ester	methanol	methylpalmitate	18.94	methyl stearate	21.04	methyl oleate	20.81

4.1.1.4 Gas chromatography–thermal conductivity detector (GC-TCD)

Qualitative analysis was carried out using GC-TCD (Focus, Thermo Scientific, Germany) equipped with a Shin Carbon ST ¹⁰⁰⁄₁₂₀ (2 m x 1 mm ID packed column, Resteck, Bellefonte, Pennsylvania). Helium was used as carrier gas. Oven temperature: 40 °C to 170 °C with rate of 20 °C min^{-1}. Samples (ca. 150 µL-Alliquote) (Hamilton, Bonaduz, Schweiz).

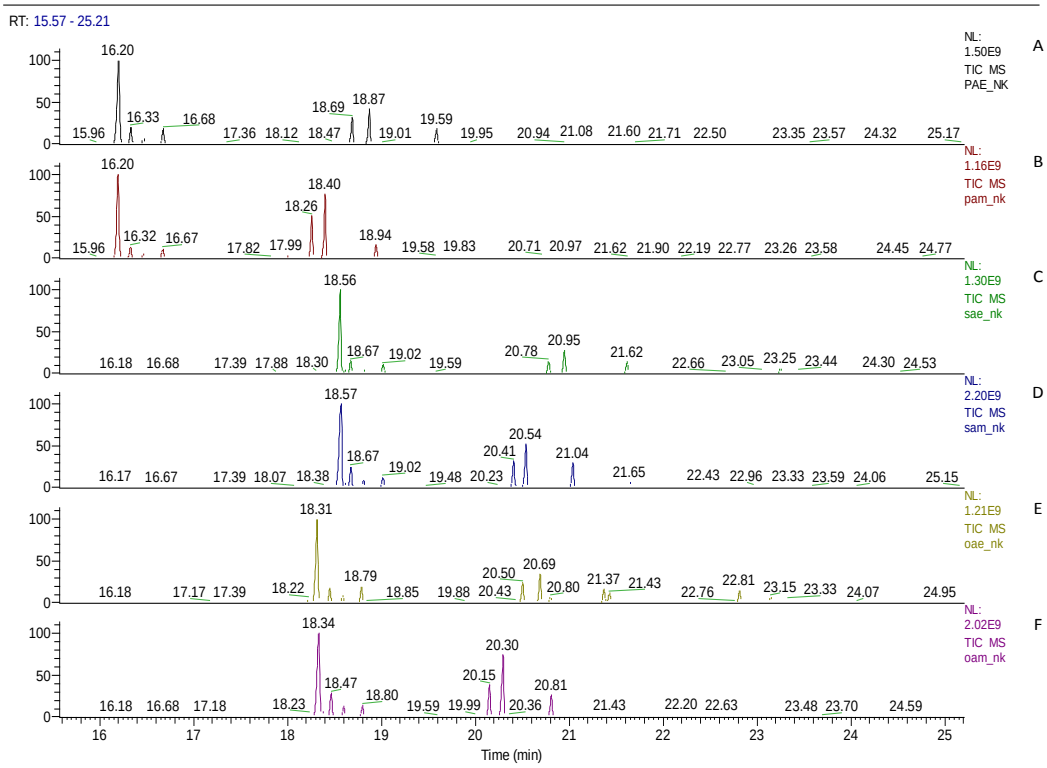

Figure 4.2: GC-MS chromatograms (A) and (B) palmitic acid; (C) and (D) stearic acid; (E) and (F) oleic acid and the respective product-mixture.

4.1.2 Chemicals

All chemicals used in this study were of analytical grade. For qualitative and quantitative analysis reference materials and solvents were used as purchased, without purification (see Table 4.2). 2,7-Octandione was produced by Kolbe-electrolysis and purified by recrystallization in heptane and confirmed by in-house NMR (1H and 13C) measurements.

Table 4.2: List of the chemicals used as standards and reagents

Chemicals	**purity**	**purchased from (Supplier)**
Reagent		
Levulinic acid (4-oxopentanoic acid)	98 %	Sigma-Aldrich, Germany
Valeric acid (pentanoic acid)	99%	Alfa Aesar GmbH & Co KG, Germany
gamma-valerolactone	99 %	Sigma-Aldrich, Germany
4-hydroxy-2-butanone	95 %	Alfa Aesar GmbH & Co KG, Germany
Formic acid	≥ 98 %	Sigma-Aldrich, Germany
Palmitic acid	98 %	Aldrich, Germany
Stearic acid	95%	Aldrich, Germany
Oleic acid	98 %	Roth, Germany
Rapeseed oil	99 %	Fluka, Germany
Acetic acid	100 %	Roth, Germany
Standard		
n-octane	99 %	Sigma–Aldrich, Germany
2-butanol	≥ 99.5 %	Sigma-Aldrich, Germany
1-butanone	≥ 99 %	Sigma-Aldrich, Germany
2-butanone	≥ 99.7 %	Sigma-Aldrich, Germany
butanoic acid	≥ 99 %	Sigma-Aldrich, Germany
1-propanol	≥ 99,9 %	Sigma-Aldrich, Germany
2-propanol	99,9 %	VWR, France
1-propanone	97 %	Sigma-Aldrich, Germany
2-octanone	98 %	Alfa Aesar GmbH & Co. KG, Germany
(±)-2-octanol	99.5 %	Sigma-Aldrich, Germany
methylvinylketon (3-buten-2-one)	95 %	Sigma-Aldrich, Germany
Propanoic acid	99 %	Sigma-Aldrich, Germany
Acetaldehyde	≥ 99.5 %	Fluka, Germany
Formaldehyde	37 % w/w in water	Sigma-Aldrich, Germany
2-methyltetrahydrofuran	≥ 99 %	Sigma-Aldrich, Germany
Pentadecane	99 %	Sigma Aldrich, Germany
1-pentadecene	99 %	Sigma Aldrich, Germany
Oleic acid methylester	99 %	Sigma Aldrich, Germany
Heptadecane	99 %	Sigma Aldrich, Germany

Table 4.3 shows all compounds applied as electrolyte additives or to produce and dilute solution, further deionized water was used for the preparation of all aqueous solutions.

Table 4.3: List of the chemicals used as electrolyte and solvents

Chemicals	**purity**	**purchased from (Supplier)**
Electrolyte		
Sulfuric acid	95 %	VWR, France
Sodium hydroxid	98 %	Riedel-de Haën, Germany
Potassium hydroxide	99.5 %	Roth, Germany
Sodium perchlorate monohydrate	≥ 98 %	Fluka, Sigma-Aldrich, Germany
solvent		
1-butanol	99.5 %	Roth, Germany
Acetone (2-propanone)	99,9 %	VWR, France
Ethanol	99.9 %	VWR, France
Methanol	99.8 %	Sigma-Aldrich Germany
Diethyl ether (ethoxyethane)	99.9 %	VWR, France
Ethyl acetate	99 %	Sigma Aldrich, Germany

4.2 Electrochemical Procedures

Target questions of the electrochemical experiments were the respective reaction course (Which product is preferentially formed (selectivity)?) as well as the Columbic efficiency relative to the applied voltage (What is the energetic efficiency of the process?). In order to analyze the electrochemical reactions more in detail potentiostatically controlled experiments were performed. These include static methods like, chronoamprometry as well as dynamic procedures like cyclic voltammetry.

4.2.1 Parameters

The educt conversion(X_i), selectivity (S_i) and yield (Y_i) of the formation of liquid products i were calculated using equations 4.1 to 4.3.

$$X_i[\%] = \frac{\Delta c_{\text{educt}}}{c_{\text{educt}}} \cdot 100 \tag{4.1}$$

$$S_i[\%] = \frac{c_i}{\Delta c_{\text{educt}}} \cdot 100 \tag{4.2}$$

$$Y_i[\%] = \frac{c_i}{c_{\text{educt}}} \cdot 100 \tag{4.3}$$

Δc_{educt} = concentration of educt i in [M]
c_i = concentration of product i in [M]
obtained from analytical methods (see Chapter 4.1)

Coulombic Efficiency

Coulombic efficiency or current efficiency *CE* describes how many electrons in form from current were transfered to the products. According to Faraday's first law of electrolysis *CE* can be calculated as shown below.

$$Q_{\text{applied}} = n_{\text{theoretical}} \cdot z \cdot F \tag{4.4}$$

$$Q_{\text{applied}} = i \cdot t \tag{4.5}$$

$$n_{\text{theoretical}} = \frac{i \cdot t}{z \cdot F} \tag{4.6}$$

$$CE[\%] = \frac{n_{\text{experimental}}}{n_{\text{theoretical}}} \cdot 100 \tag{4.7}$$

Q = Charge [A s], if current is not constant over the time, charge is the integral of current with time
i = current [A]
z = number of transferred electron per molecule
$n_{\text{experimental}}$ [mol] is obtained from analytical methods (see Section 4.1)

If the identification or quantification of the products are not possible a first estimations of Coulombic efficiency CE_X can be done considering the educt conversion. Here is assumed that all reactions of starting materials are due to the action of the current which must be checked in particular cases. The use of Coulombic efficiency based on educt conversion is uncommon, but it can be helpful for initial estimations. It should be clear that the error of CE_X is always greater than that of the other parameters, since for its calculation, the number of electrons transfered z has to be estimated.

The term "Farad equivalent" is used to express the applied electric charge in relation to the theoretical charge (according to Faraday's law). For example, for the conversion of 5 mmol of fatty acid into the non-Kolbe products, 965 coulomb (= 5 mmol x 2 x 96485 C mol^{-1} are needed and correspond to 1 Farad equivalent and hence a charge of 1930 C corresponds to 2 Farad equivalent.

A further relevant parameter for the evaluation of reactions in flow systems is the residence time (τ), defined as $\tau = \frac{V}{\dot{V}}$[s], where V=reactor volume [m^3] and $\dot{V}$= volumetric flow rate [$\text{m}^3\,\text{s}^{-1}$].

General Equipment: All electrochemical reactions were conducted under potentiostatic control using an AMEL 7050 potentiostat (Amel srl, Milano, Italy), a SP50 potentiostat (Bio-Logic SAS, Claix, France) or a Princeton Potentiostat/Galvanostat Model 273A (Princeton, USA). A three electrode configuration was used and E_{WE} stands for the potential applied at the working electrode and E_{CE} for potential measured at the counter electrode. Ag / AgCl sat.KCl

reference electrodes (SE11, Sensortechnik Meinsberg, Germany, 0.195 V *vs.* SHE) were used through this work for batch experiments. All electrode potential in this work are reported versus this electrode, but are normalized to standard hydrogen electrode for energetic calculations.

Electrode Materials: As anode or cathode material for reactions presented in Section 4.2.2 and Section 4.2.3 following materials were used: graphite foil (chemPUR, Germany), polycrystalline graphite sheet (SGL Carbon GmbH, Germany), graphite felt (SGL Carbon GmbH), lead sheet (99.999 % , chemPUR), and platinum sheet (99.9 %, chemPUR).

A pretreatment procedure was applied to remove contaminants from the electrode surfaces. The lead electrodes were rinsed in 25 % HNO_3, treated with sand paper (grain size 8000) and washed with deionized water. Graphite felt electrodes were washed with deionized water and used directly. Platinum electrodes were pretreated by flame annealing and washed with deionized. All the others electrodes were washed in HCl, treated with sand paper and washed with deionized water.

4.2.2 Levulinic Acid Conversion

A detailed overview on all performed reactions is shown in Table 5.1 and Table 5.2 and results for exemplary reactions are presented in 5.

Electroorganic Synthesis in Batch System: As electrochemical cells for batch reactions one chamber undivided glass cells with 50 mL reaction volume and a two-chamber H-type electrochemical glass cell (as shown in Nilges and Schröder 2013) with respectively 40 mL anode and cathode chambers separated via a cation exchange membrane (fumasep® FKE, Fumatech, Germany) was used, with electrode size varying from 5 cm^2 to 24 cm^2. All reported current densities are normalized to the geometric surface area.

Electroorganic Synthesis in Continuous Flow System: The electrochemical flow cells were a costum-made Plexiglas® cell with 21 mL reaction volume (11 cm^2 anode and cathode area) and a the commercial flow cell *Micro Flow Cell* (ElectroCell, Denamark) with 20 mL reaction volume and 10 cm^2 for anode and cathode. The cells were operated in or single-pass or recirculation mode as illustrated in Figure 4.3. Configuration (A) was a electrochemical reactor consisting of two chambers, an anode and a cathode chamber divided by a membrane. Anolyte and catholyte were both recirculated through the corresponding tank using a peristaltic pump. At (B) the reactor was operated without membrane and without recirculation and at (C) the reactor was operated without membrane but with recirculation of the reaction solution. A combination of different configurations is also possible.

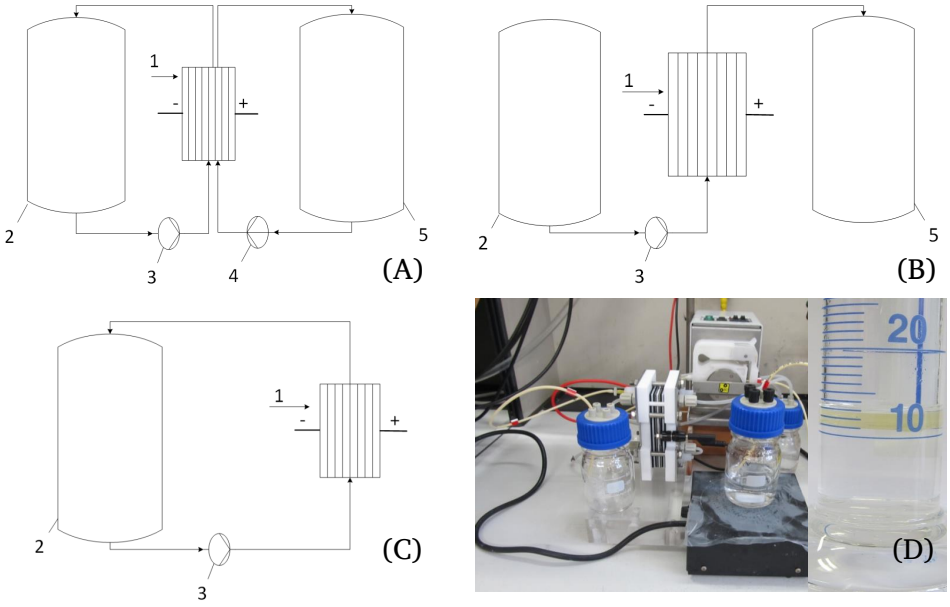

Figure 4.3: Experimental set-up: (A) with recirculation (anode and cathode chamber separated), (B) single-pass, (C) one chamber with recirculation, (1) electrochemical reactor, (2) and (5) tanks, (3) and (4) peristaltic pumps. (D) picture of the system and of the phase separation of the products (route *VII*, see Figure 5.1)

The circulation volume varied with experiments from 25 mL to 250 mL. Prior to the each experiment, tightness of the electrochemical cell was checked. Then, electrochemical synthesis was performed galvanostatically or potentiostatically. at flow rates between 0.36 mL min to 10 mL min (thus the hydraulic residence time varies from 6 s to 3600 s). The duration of the electrolysis experiments varied according with initial concentration and achieved current.

4.2.3 Fatty acids and Triglycerides Conversion

All electrochemical experiments were conducted using undivided glass cells of 40 mL to 100 mL volume. All electrolysis experiments were performed until a charge of 2 or 4 F mol^{-1} (as indicated) of fatty acids equivalents was passed. Cyclic voltammetry was performed using a scan rate of 20 mV s^{-1}.

For electrolysis in organic solvents 0.025 mol L^{-1} to 0.25 mol L^{-1} of fatty acids or rapeseed oil (here in 0.025 mol L^{-1} to 0.25 mol L^{-1} of fatty acid equivalents) in methanol or ethanol were prepared and equimolar amounts KOH were added and galvanostatic electrolysis at mA (equaling current densities of 17 mA cm^{-2}) was conducted under continuous stirring.

For electrolysis in aqueous solutions 0.025 mol L^{-1} to 0.25 mol L^{-1} of fatty acids or rape-

seed oil (here in 0.025 mol L^{-1} to 0.25 mol L^{-1} of fatty acid equivalents) in deioniezed water were prepared and equimolar amounts KOH were added. As the fatty acids and triglycerides are only sparingly soluble in water, the experiments were performed using ultrasound (Ultrasonic Processor UP400S (Hielscher Ultrasonics GmbH, Germany), 400 W, ultrasonic frequency 24 kHz). The resulting emulsion systems were electrolyzed potentiostatically at 3 V at the working electrode. Notably, the emulsion was stable during the experiment and thus emulsion breaking using concentrated sulfuric acid was necessary prior to quantitative analysis.

5 | Electrochemical Levulinic Acid Conversion [1]

This chapter presents the routes for primary and secondary electrochemical conversion reactions of levulinic acid, including both oxidative and reductive pathways. Figure 5.1 summarizes the reactions investigated in this study. The derived products may either find direct application as fuels or solvents or may serve as intermediates for further processes — which have been show in Table 2.1.

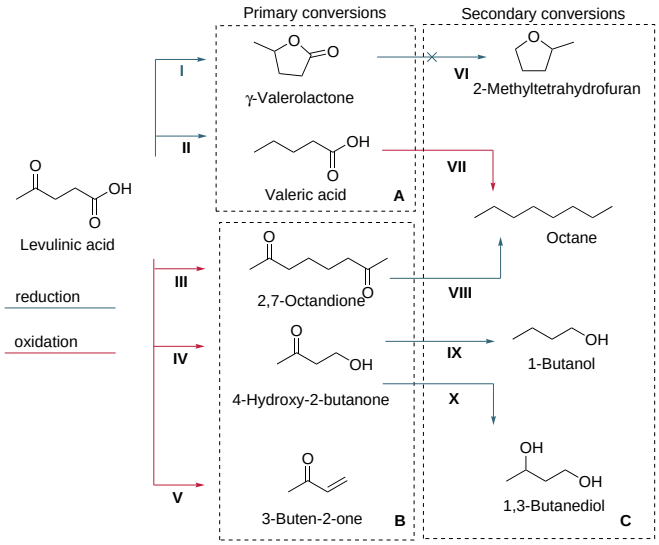

Figure 5.1: Schematic illustration of the pathways for the primary and secondary electrochemical conversion of levulinic acid. A) electrochemical reduction of levulinic acid, B) electrochemical oxidation from levulinic acid and C) electrochemical conversion of the primary reactions products

[1]This chapter has been published as **Santos, T. R. d.**, Nilges, P., Sauter, W., Harnisch, F., and Schröder, U. Electrochemistry for generation of renewable chemicals: Electrochemical conversion of levulinic acid. RSC Adv., 5:26634-26643, 2015. This publication contains results from the dissertation of Peter Nilges entitled: Conversion of levulinic acid and furfurals as renewable resources into chemicals and biofuels using electrochemical synthesis and from the Master-thesis of Waldemar Sauter entitled: Auswirkungen des Elektrodenmaterials auf die elektrokatalytische Hydrierung von Lävulinsäure. However, the author of this work - and first author of the RSC-Advances publication - was responsible for the design and execution of the majority of experiments, data collection and data interpretation as well as manuscript writing.

5.1 Primary Conversion: Reduction of Levulinic Acid to Valeric Acid and $\gamma-$valerolactone (A)

Figure 5.2 shows the electrochemical reduction pathways of LA. Selected conditions have already been investigated by several authors, e.g. Xin et al. 2013. The present study investigate systematically the impact of a variety of electrode materials, the electrolyte composition and the educt concentration on the LA reduction.

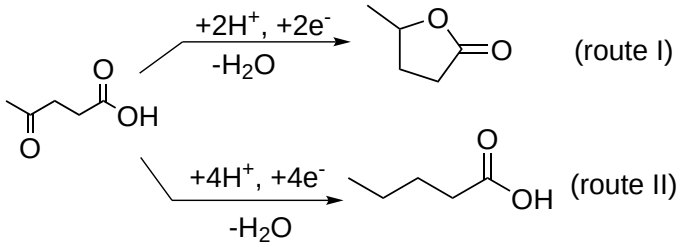

Figure 5.2: Reaction pathways of the electrochemical reduction of levulinic acid to *(I)* γ-valerolactone and *(II)* valeric acid (Part *A* of Figure 5.1)

Figure 5.3 summarizes the results of the levulinic acid reduction as a function of initial educt concentration. Changing the educt concentration does not affect the selectivity of the product formation: at a Pb electrode in 0.05 mol l^{-1} H_2SO_4 electrolyte solution, and an applied working electrode potential of -1.8 V, valeric acid is always the main product. The increase of the initial educt concentration has, as expected, a positive impact to the Coulombic efficiency (*CE*) (see Section 4.2). At sufficiently high levulinic acid concentration the hydrogenation process is the dominating reaction; whereas at low educt concentrations hydrogen evolution via water electrolysis as the main side reaction prevails, leading to low Coulombic efficiency and LA hydrogenation rate. Consequently, when using a levulinic acid starting concentration of 0.5 mol l^{-1} instead of 0.05 mol l^{-1} , the average conversion rate increases from 3.3 mg cm^{-2} h^{-1} to 29.5 mg cm^{-2} h^{-1} and the achieved *CE* increases from 6 % to 60 %. A LA concentration of 0.5 mol l^{-1} represents an optimum value, since a further increase of the starting concentration does not lead to a further significant increase of conversion rate and *CE*.

Besides the Coulombic efficiency aspect, it is of special interest to achieve high product concentrations for the conversion of levulinic acid to valeric acid (see Figure 5.2 - route *(II)*, since spontaneous product separation can be achieved when the saturation concentration of 0.39 mol l^{-1} is exceeded (see inset picture in Figure 5.3).

Electrochemical conversions are heterogeneous processes, and as such their mechanisms are decisively determined by the nature of the electrode material. Figure 5.4 summarizes major parameters of the levulinic acid reduction as a functions of the used electrode material and nature of the electrolye. In 0.5 mol l^{-1}, lead stands out clearly over the other electrodes

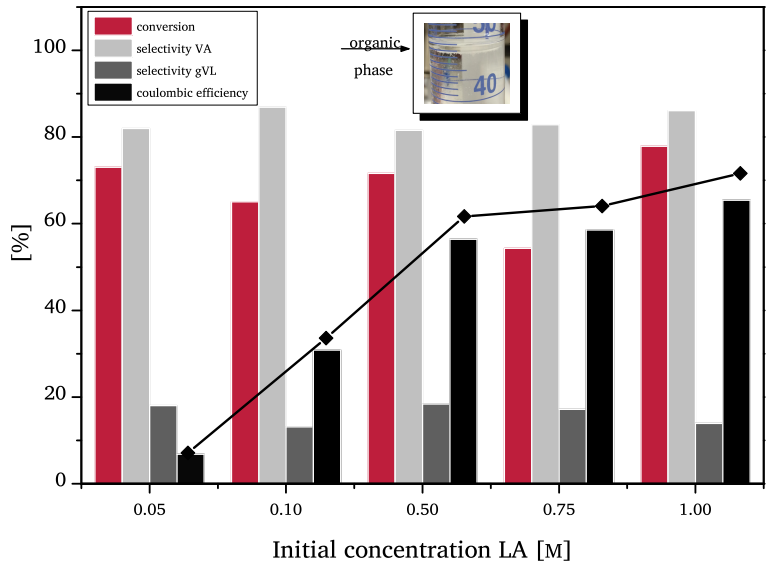

Figure 5.3: Electrocatalytic hydrogenation of levulinic acid at Pb-Electrode in a devided H-Cell, at different initial concentration of levulinic acid after 4 h to 8 h hours electrolysis at a potential of -1.8 V. The formation of the organic product phase is shown in the insert picture. Details can be found in Table 5.1 entry *1* to *17*

in terms of educt conversion to valeric acid and Coulombic efficiency. This performance may be explained by to the higher overpotential of the hydrogen evolution reaction at Pb-cathodes, since at Cu, Fe and Ni the water electrolysis commences already at an electrode potential of -1 V.

When switching the cathode material from lead to carbon in acidic electrolyte, the hydrogenation of levulinic leads almost exclusively to the formations of γ-valerolactone (gVL). A conversion of 40 % was obtained, which represents a ten-fold improvement as compared to the previous work by Xin et al. 2013. The selectivity of the gVL formation is 68 %. Whereas gVL is formed in sulfuric acid solutions at Cu and Ni electrodes, no formations of valeric acid was observed in alkaline solution at this electrode materials. In alkaline solution gVL is the major product only when Pb and Fe electrodes are used. For the electrochemical conversion of LA to gVL at Pb electrode a Coulombic efficiency of 21 % can be achieved, whereas the use of Fe cathode results in a slightly lower Coulombic efficiency (18 %), but a higher selectivity. For this reason, and especially with regard to the sustainability of the process, Fe and C are very promising alternatives as electrode material for further investigations. It is very likely, that Coulombic efficiency can be enhanced when using higher initial educt concentrations or when operating in a continuous system.

In summary, VA and gVL can both be obtained from LA with good selectivity and acceptable Coulombic efficiency.

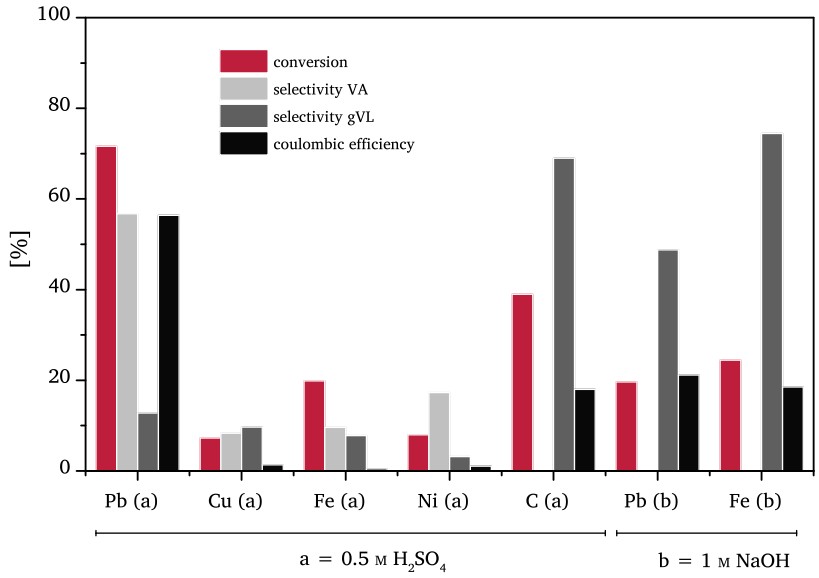

Figure 5.4: Electrocatalytic hydrogenation of levulinic acid in a devided H-Cell as a funtion of the nature electrode material and electrolyte. The data are based on 2-4 hours electrolysis at an electrode potential of -1.8 V, the initial *LA* concentration was 0.5 mol l^{-1}

5.2 Primary Conversion: Oxidation of Levulinic Acid to 2,7-octanedione, 4-hydroxy-2-butanone and 3-buten-2-one (B)

Whereas the reductive conversion of levulinic acid may potentially be directly used for energy storage processes (see also Chapter 7), the oxidation of levulinic acid is of primary interest for chemical production. Levulinic acid can be oxidezed either to a keto-alkyl (one electron oxidation) or to a carbenium ion (two-electron oxidation) (see Figure 5.5). Thereby the Kolbe product of LA, the dimer 2,7-octadione, yields from the radical and its subsequent dimerization (route *III*) as presented in our previous work (Nilges et al. 2012), further examples for the application of this reaction using other coumpounds have been widely investigated by Conway and Vijh 1966; Schäfer 1979, 1990; Vijh and Conway 1966. The carbenium ion, product of the two-electron oxidation, on the other hand, may react further either with a nucleophiles like hydroxide ions (Non-Kolbe reaction or Hofer-Moest-reaction, as shown by H. Hofer and Moest 1902; Klocke et al. 1993; Miller and J. Hofer 1984), yielding 4-hydroxy-2-butanone (route *IV*), or may undergo an elimination of H^+ , forming 3-buten-2-one (route *V*) (Walton 2002).

One-electron Oxidation: Formation of 2,7-Octandione (route III)

2,7 octandione can be gained with good selectivity and a good *CE* in methanol electrolyte solution, using platinum electrodes. If water is used as solvent the consequences were a de-

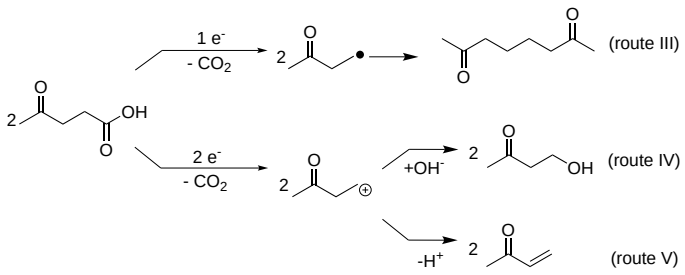

Figure 5.5: Reaction pathways of the electrochemical oxidation of levulinic acid

crease of the selectivity and significant impact on the Coulombic efficiency, decreasing from 86 % in methanol to 5 % in aqueous solution (see Table 5.1). This was not unexpected, since in aqueous solution the current density was higher, promoting a stronger solvent decomposition. Here, the increase of he initial levulinic acid concentration could not compensate this effect. Furthermore, aqueous solutions stabilized ionic specis like two-electron oxidation product carbenium ion, which leads to the formation of multiple side products. The formation of side products explains the lower selectivity (27 %) in comparison to methanol (60 %) even at higher conversions of levulinic acid (74 %).

Two-electron Oxidation: 4-hydroxy-2-butanone (route IV) and 3-buten-2-one (route V)

The formation of the carbenium ion by the two-electron oxidation of LA can be generally enhanced by the use of a graphite anode instead of platinum, as at Pt radical adsorption promotes dimerization (Schäfer 1990) . The reactions were first conducted in a batch reactor in an aqueous $0.2\,\mathrm{mol\,l^{-1}}$ electrolyte solution using a carbon sheet anode. In alkaline solution carbenium ions are captured by hydroxide ions, leading to the formation of 4-hydroxy-2-butanone (route *IV*). At an anode electrode potential of 6 V a selectivity of 20 % and a Coulombic efficiency of 5 % was obtained. Noteworthy, to our knowledge it its the first time that the direct production of this compound from levulinic acid is presented. In addition to this non-Kolbe product only minor amounts of side products including the Kolbe product (2,7-octadione) and 2-butanone were identified. When the above reaction is performed in alcoholic solution (Eberson and Nyberg 1976; Wladislaw and Viertler 1968), alkoxide ions serve as nucleophile; thus the reaction product is the respective ether. We have confirmed the formations of 4-methoxy-2-butanone and 4-ethoxy-2-butanone in methanol and ethanol electrolyte solution (data not shown). Interestingly, when performing the reaction in a membrane separated flow cell, the major oxidation product is 3-buten-2-one (Figure 5.5, route *V*). This finding (Table 5.1, raw 15 and 16) can so far not be explained and has to be studied further.

Table 5.1: Reactions conditions and main results for primary reductive and oxidative conversion

	route	educt [mol l^{-1}]	electrode	E_{WE} [V]	t [h]	electrolyte solution	X [%]		S [%]		CE [%]
		LA					LA	gVL	VA		
1	*I,II*	0.05	Pb	-1.8	4	0.5 mol l^{-1} H_2SO_4	73.0	18.0	82.0		6.8
2	*I,II*	0.1	Pb	-1.8	4	KH_2PO_4/K_2HPO_4	–	–	–		–
3	*I,II*	0.1	Pb	-1.8	4	0.5 mol l^{-1} H_2SO_4	65.1	13.1	86.9		30.9
4	*I,II*	0.50	Pb	-1.8	4	0.5 mol l^{-1} H_2SO_4	71.6	18.4	81.6		56.4
5	*I,II*	0.75	Pb	-1.8	8	0.5 mol l^{-1} H_2SO_4	54.3	17.2	82.8		58.6
6	*I,II*	1.00	Pb	-1.8	4	0.5 mol l^{-1} H_2SO_4	77.9	13.9	86.1		65.4
7	*I,II*	0.50	Cu	-1.8	4	0.5 mol l^{-1} H_2SO_4	7.3	9.6	8.3		1.3
8	*I,II*	0.50	Fe	-1.8	4	0.5 mol l^{-1} H_2SO_4	19.9	7.8	9.6		0.5
9	*I,II*	0.50	Ni	-1.8	4	0.5 mol l^{-1} H_2SO_4	8.0	3.2	17.3		1.1
10	*I,II*	0.50	C	-1.8	4	0.5 mol l^{-1} H_2SO_4	39.0	69.0	0.0		18.0
11	*I,II*	0.50	Pb	-1.8	4	0.5 mol l^{-1} NaOH	19.6	48.7	0.0		21.1
12	*I,II*	0.05	Pb	-1.8	4	1.0 mol l^{-1} NaOH	24.5	74.5	0.0		18.5
								2.7-OD	4H2B	MVK	
13	*III*	1.00	Pt	5.0	7	Methanol, pH 5.5	60.0	47.0	–	–	86.2
14	*III*	1.00	Pt	5.0	7	H_2O, pH 5.5	74.0	27.0	–	–	5.0
15	*IV*	0.1	C	6.0	5	0.2 mol l^{-1} NaOH	57.0	–	20.0	–	5.0
16	*IV*	0.1	C	1–3	5	0.1 mol l^{-1} NaOH	74.0	–	–	45.0	24.0
17	*V*	0.1	C	2–3	6.5	0.1 mol l^{-1} H_2SO_4	42.0	–	–	18.0	8.0

5.3 Secondary Electrochemical Conversion Steps (C)

The products of the primary LA conversion can be used as educt for secondary electrochemical conversion steps (see Figure 5.1 — secondary conversions). Some of these reactions, as the production of n-octane by the reduction of 2,7-octandione and the Kolbe-coupling of valeric acid are reported in the following sections. Further, the hydrogenation of gVL (Figure 5.1, route *VI*) is very appealing, but unfortunately could not be experimentally proven.

Electrochemical Hydrogenation of 4-hydroxy-2-butanone (route IX and X)

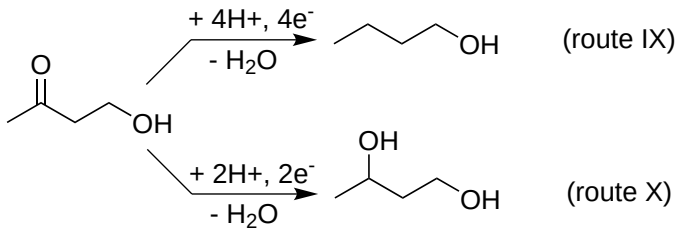

Figure 5.6: Reaction pathways of the electrochemical hydrogenation of 4-hydroxy-2-butanone

The electrocatalytic hydrogenation of 4-hydroxy-2-butanone (4H2B) was performed at Pb electrodes in aqueous 0.5 mol l^{-1} H_2SO_4 electrolyte solution. After 3.5 h of electrolysis, 85 % conversion of 4-hydroxy-2-butanone was achieved and 1-butanol was gained with 84 % selectivity. At 100 % conversion 1-butanol is gained with 75 % yield and with a Coulombic efficiency of 29 %. 1,3-butandiol was founded as the only side product. For the use of other electrode materials both conversions rate and Coulombic efficiency were lower (comparable to the results found for the hydrogenation of levulinic acid) and 1,3-butandiol was produced only with low selectivity (not higher than 10 %). As for the hydrogenation of levulinic acid, the Coulombic efficiency of the 4H2B hydrogenation can be significantly improved by higher educt concentration. Thus, the Coulombic efficiency of 1-butanol formation increased from 13 % for a 0.08 mol l^{-1} solution to 52 % using a 0.5 mol l^{-1} 4-hydroxy-2-butanone solution. In order to achieve a higher selectivity of 1,3-butandiol formation, the hydrogenation of 4H2B was studied using different electrolytes and different electrode materials. Here, the use of phosphate (0.5 mol l^{-1}, pH 7) and iron electrodes yielded the highest 1,3-butandiol selectivity of 34 % (see Table 5.2).

Oxidation of Valeric acid to n-octane (route VII)

As known from literature and confirmed by previous work from our group (Nilges et al. 2012), the Kolbe reaction proceeds preferably at high current density and high educt concen-

Table 5.2: Reactions conditions and main results for secondary reductive conversions

	route	educt [mol l^{-1}]	cathode	E_{WE}	t	electrolyte solution	C	S		CE
				[V]	[h]		[%]	[%]		[%]
		4H2B					4H2B	1-BuOH	1,3-BDO	
1	*IX,X*	0.08	Pb	-1.3	3.5	0.5 mol l^{-1} H_2SO_4	17.8	15.9	0.4	16.8
2	*IX,X*	0.08	Pb	-1.5	3.5	0.5 mol l^{-1} H_2SO_4	65.1	71.5	2.6	12.7
3	*IX,X*	0.08	Pb	-1.8	3.5	0.5 mol l^{-1} H_2SO_4	68.8	55.6	1.7	8.0
4	*IX,X*	1.00	Pb	-1.5	3.5	0.5 mol l^{-1} H_2SO_4	19.2	58.0	2.5	59.5
5	*IX,X*	0.08	Fe	-1.5	4	KH_2PO_4/K_2HPO_4	23.9	0.0	23.1	2.1
6	*IX,X*	0.08	Fe	-1.8	4	KH_2PO_4/K_2HPO_4	34.4	0.0	34.7	2.4
7	*IX,X*	0.08	Pb	-1.8	4	KH_2PO_4/K_2HPO_4	9.8	19.3	0.7	2.1

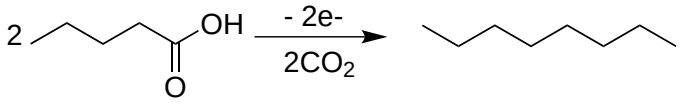

Figure 5.7: Reaction pathways of the electrochemical oxidation VA of n-octane

tration - both factor promoting the formation of high keto alkyl radical concentrations at the electrode surface and thus to the production of the dimer - in this case n-octane. Additional to n-octane, this organic phase contains the side products butyl-valearate and 1-butanol. Wadhawan proposed a possible mechanism for the production of esters during of the Kolbe electrolysis in aqueous solution (Figure 5.8) (J. D. WADHAWAN et al. 2001). This scheme illustrates that butyl-valearate is formed, when only one CO_2 is cleaved, whereas the formation of n-octane requires the complete elimination of both CO_2 .

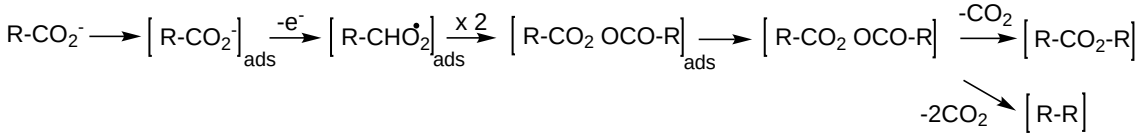

Figure 5.8: Potential mechanism for the formation of n-octane and butyl-valerate during Kolbe electrolysis (derived from J. D. WADHAWAN et al. 2001)

The side product 1-butanol is generated via a Hofer-Moest reaction by a two-electron oxidation of valeric acid and the formation of a carbenium ion that reacts with a hydroxide ion to form 1-butanol. The side product formation is dependent on the starting concentration of valeric acid and on the reactor configuration. In order to suppress this kind of side-reactions, experiments in a flow reactor were performed (as described in Figure 4.3 and presented Table 5.3). Compared with the results for batch reactors, the Coulombic efficiency could not be improved with this setup, but even for a non-optimized system a *CE* of 50 % was reached. A further improvement can be achieved when using a flow reactor (see Figure 4.3), as the selectivity of n-octane increases from 51 % to 81 %. The higher selectivity may result par-

ticularly from the lower residence time, which was for batch systems at least 4 h, whereas a residence time not longer than 5 min, preventing further reactions, was realized in flow-through reactors. For this reactions pathway the main product is insoluble in the electrolyte solution, which allows a direct separation of the product and electrolyte reuse in a continuous process.

Table 5.3: Overview of different galvanostatic guided electrochemical experiments with various carboxylic acids in analogy to the experimental setup described in Figure 4.3

Nr	Educt	Concentration [$g\,L^{-1}$]	Set-up	Flow rate [mL min]	Conversion [%]	CE
1	butyric acid	22	B	0.7	67	19
2	butyric acid	88	B	0.7	52	73
3	butyric acid	44	C	0.7	56	23
4	butyric acid	176	C	0.7	35	34
5	butyric acid	176	C	0.7	24	24
6	iso-valeric acid	26	C	0.7	65	18
7	valeric acid	51	A	4	95	58
8	valeric acid	102	A	100	30	53
9	valeric acid	200	B	4	83	50

Two-electron Oxidation and the Non-Kolbe Reaction of Valeric acid

Within this investigation a non-Kolbe reaction based decomposition of valeric acid (see Figure 5.9) was studied and the difficulty to control the product formation is demonstrated. When the electrochemical conversion of short chain fatty acids, like valeric acid, is performed at carbon instead of platinum electrodes, the reaction leads to the formation of carbenium cations via a two-electron oxidation (route *VII*). These cation can then be attacked by a respective nucleophile (in water the hydroxide ion). Thus, the electrolysis of valeric acid at the carbon anode in aqueous environment ($0.5\,mol\,l^{-1}$ H_2SO_4) leads to the formation of alcohols. Depending on the location of the positive charge at the carbenium ion the hydroxide ion can attack either at position 1 (to form 1-butanol) or at position 2 (to form 2-butanol). At the applied positive anode potential a further oxidation of these products takes place: 1-butanol is oxidized to butanal, 2-butanone is oxidized to 2-butanol. Whereas ketones are inert to further oxidation, the aldehyde can be oxidized to carboxylic acids - which again can be decarboxylated in a further oxidation cycle. Thus — as illustrated in Figure 5.9 — a successive shortening of the carbon chain occurs, leading to carbon dioxide as the final product. In order to control the reaction and to prevent the successive decomposition, a charge transfer from a primary to secondary carbenium ion is necessary. The secondary carbenium ions will react with hydroxide ion to a secondary alcohol and thus no further oxidation than to the ketone is possible. Such control of the reaction did not succeed in full

extent and the use of large electrolyte ions to stabilize the carbenium ion did not lead to the desired success.

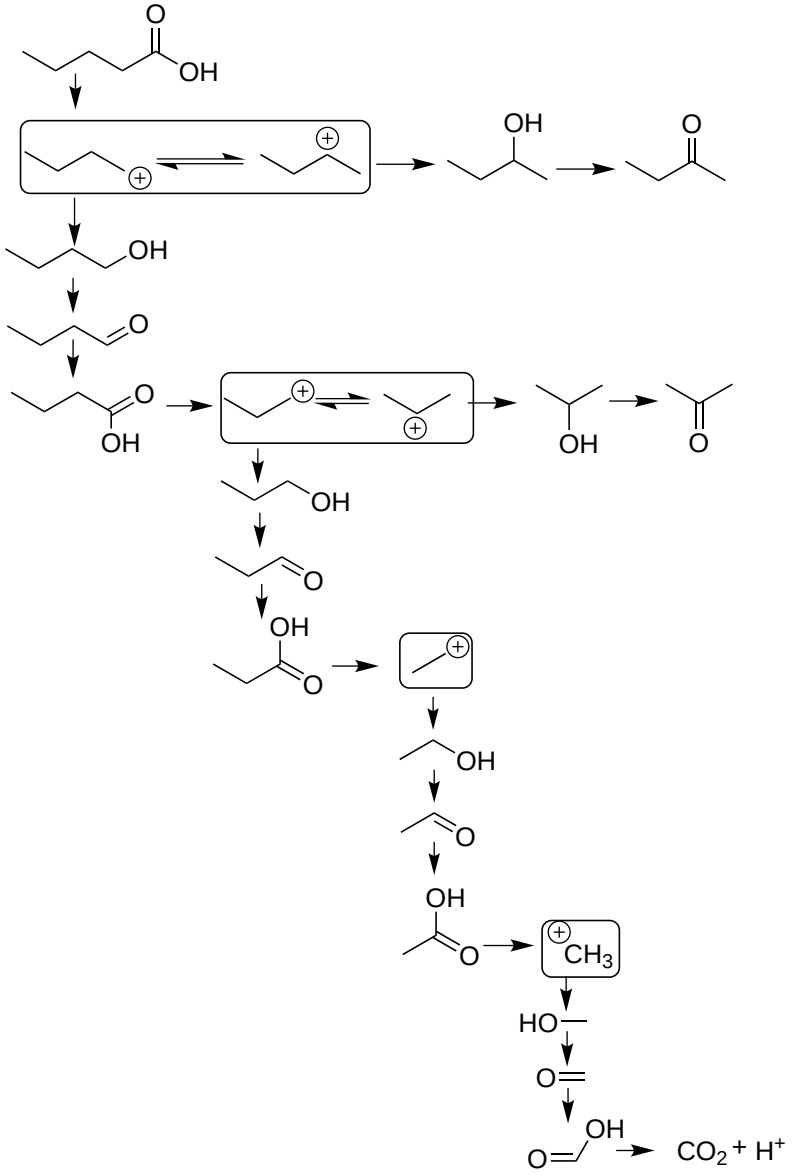

Figure 5.9: Anodic degradation of valeric acid at graphite electrodes

As depicted in Figure 5.10, the proposed in Figure 5.9 degradation can be experimentally confirmed. Depending on the reaction time (and thus the degree of valeric acid conversion) the major reaction products and intermediates could be found.

The experiment also confirms the accumulation of 2-butanone - the product of the secondary carbenium ion. Interestingly, no acetone was detected through the experiments, which indicates that the primary propyl carbocation very quickly reacts to the primary alcohol, before the secondary carbenium ion is formed. The addition of other electrolytes species, however, did not have any significant impact on the course of the reaction (see Table 5.4). Another alternative for the selective conversion of valeric acid via non-Kolbe electrolysis could be

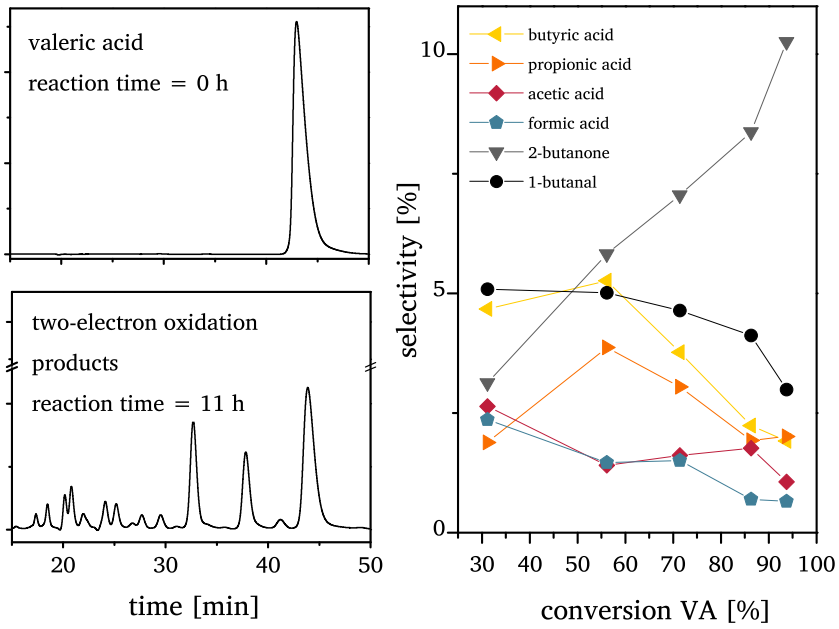

Figure 5.10: HPLC-chromatograms and the quantitative product analysis of a valeric acid (50 M) non-Kolbe electrolysis (performed at a graphite electrode in 50 mM NaOH solution, at a potential of 2.5 V and a current density of 2.5 mA cm^2

achieved using a flow reactor. First experiments indicates, that 2-butanol can be obtained as main product (see Figure 5.11 and Figure 5.12), probably an effect of the lower contact time of products with the electrode surface.

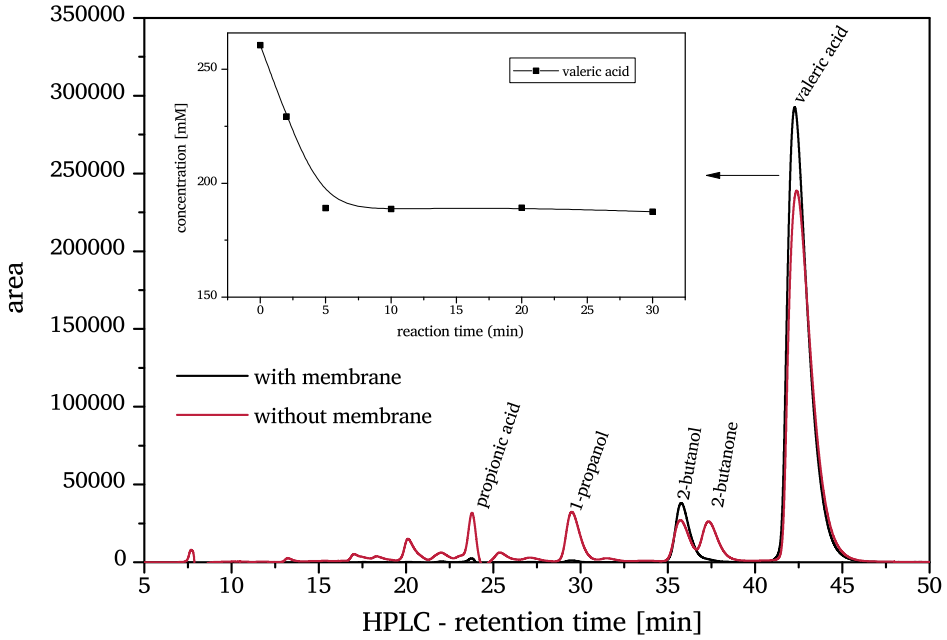

Figure 5.11: Valeric acid conversion using a flow reactor (see Figure 4.3), product formation with and without membrane

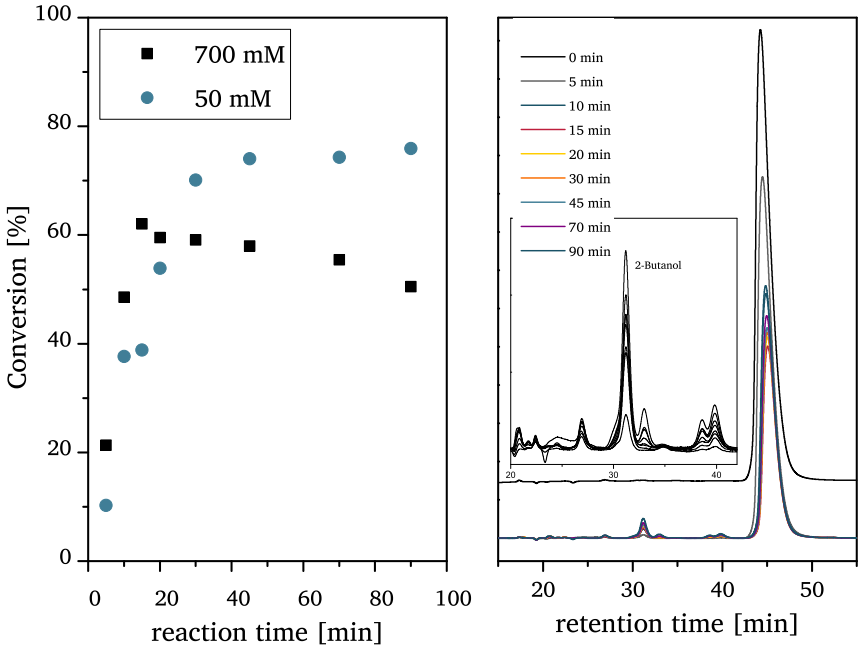

Figure 5.12: Valeric acid reaction at a microflow cell(see Figure 4.3)

Table 5.4: Reactions conditions and main for secondary oxidative conversion of the anodic oxidation of valeric acids at different graphite electrodes

entry	educt concentration [mol l^{-1}]	electrode material	E_{WE} [V]	t [h]	electrolyte solution	current density [mA cm^{-2}]	X [%]	S [%]
1	0.21	C_{sheet}	2.5	6	Water	10	90	12
2	0.22	C_{sheet}	2.5	6	0.5 mol l^{-1} H_2SO_4	10	98	19
3	0.23	C_{sheet}	2.5	6	0.25 mol l^{-1} $NaOH$	10	98	18
4	0.25	C_{sheet}	2.5	10	0.25 mol l^{-1} $NaOH$	5	56	18
5	0.24	C_{sheet}	2.5	19	0.25 mol l^{-1} $NaOH$	1	35	22
6	0.25	C_{sheet}	2.5	10	0.75 mol l^{-1} $NaOH$	25	79	18
7	0.25	C_{sheet}	2.5	10	0.75 mol l^{-1} $NaOH$	10	52	4
8	0.25	C_{sheet}	2.5	10	0.75 mol l^{-1} $NaOH$ \ 0.75 mol l^{-1} $NaHCO_3$	10	53	4
9	0.20	C_{sheet}	2.5	11	0.75 mol l^{-1} $NaOH$ \ 0.25 mol l^{-1} $NaHCO_3$	25	64	13
10	0.23	C_{sheet}	2.5	7	0.75 mol l^{-1} $NaOH$ \ 0.25 mol l^{-1} $NaHCO_3$	45	78	26
11	0.25	C_{sheet}	2.5	13	0.75 mol l^{-1} $NaOH$ \ 0.10 mol l^{-1} $NaHCO_3$	45	95	16
12	0.22	C_{sheet}	2.5	11	0.25 mol l^{-1} H_2SO_4 \ 0.5 mol l^{-1} $NaClO_4$	7.5	83	13
13	0.22	C_{sheet}	2.5	11	0.25 mol l^{-1} $NaOH$ \ 0.5 mol l^{-1} $NaClO_4$	25	99	11
14	0.22	C_{sheet}	2.5	2	0.25 mol l^{-1} $NaOH$ \ 0.5 mol l^{-1} $NaClO_4$	45	77	7
15	0.21	C_{sheet}	2.5	2	0.25 mol l^{-1} $NaOH$ \ 1.0 mol l^{-1} $NaClO_4$	45	73	8
16	0.22	C_{sheet}	2.5	10	0.25 mol l^{-1} $NaOH$ \ 0.5 mol l^{-1} Na_2SO_4	5	72	10
17	0.22	C_{foil}	2.5	2	0.25 mol l^{-1} $NaOH$	80	99	17
18	0.22	C_{felt}	2.5	2	0.25 mol l^{-1} $NaOH$	80	92	16
19	0.25	C_{sheet}	2.5	2	0.25 mol l^{-1} $NaOH$	80	98	16
20	0.25	C_{sheet}	2.5	10	0.35 mol l^{-1} $NaOH$	10–25	93	13
21	0.25	C_{sheet}	2.5	10	0.35 mol l^{-1} $NaOH$	2–5	55	15
22	0.01	C_{sheet}	2.5	8	0.01 mol l^{-1} $NaOH$ \ 0.1 mol l^{-1} $NaClO_4$	10	90	18
23	0.04	C_{sheet}	2.5	12	0.05 mol l^{-1} $NaOH$ \ 0.1 mol l^{-1} $NaClO_4$	10	95	21
24	0.04	C_{sheet}	2.5	7	0.05 mol l^{-1} $NaOH$	2.5	94	28
25	0.04	C_{sheet}	2.5	7	0.05 mol l^{-1} $NaOH$	10	99	26

6 | Fatty Acids and Triglycerides Conversion[1]

Following the concepts of biorefineries the proposed methods for biofuel production using electrochemical decarboxylation is in principle applicable to a large variety of fatty acids and triglycerides, present in different natural resource ranging from vegetable oils via animal fats to algae KNOTHE 2011. In order to demonstrate its principle applicability and thereby proof the suitability of electrochemistry as (part of) the biorefinery, the following exemplary free fatty acid were chosen for this study: i) stearic acid (C_{18} saturated: octadecanoic acid) and ii) oleic acid (C_{18} mono-unsaturated; (9Z)-Octadec-9-enoic acid) as well as the triglyceride rapeseed oil (BIERMANN et al. 2000). Thereby the decarboxylation of free fatty acids is demonstrated in organic solvents whereas for the transformation of triglycerides is shown in aqueous emulsions using sonoelectrochemistry. Figure 6.1 and Table 6.1 summarize the main findings of this study that are discussed in detail in the following sections.

Table 6.1: Summary of the investigated electrochemical conversions depicted in Figure 6.1. The experiments *A*, *B*, *C* and *D* were performed galvanostatically at a current density of 17 mA cm^{-2} (per geometric anode surface area). The experiments *E* and *F* were performed potentiostatically at 3 V

	starting material	**solvent**	**electrochemical products**	**byproducts**	**restrictions**
A	fatty acid [1]	methanol ethanol	alkene + ether	ester	none
B	fatty acid		water [3]	-	foaming
C	fatty acid glycerol [2]	methanol ethanol	alkene + ether	ester	none
D	fatty acid glycerol [2]	water	-	-	fatty acid do not react
E	triglyceride	water	alkene	-	sonoelectrochemistry
F	triglyceride	methanol ethanol	[4]	ester	transesterification

[1]Oleic acid and stearic acid were used as representative fatty acids, [2]Mixture, simulation of complete hydrolysis of a triglyceride, [3] Due to uncontrollable foam formation the electrolysis of long chain free fatty acids in aqueous medium was unsuccessful, [4]The electrolysis of triglycerides in organic solvents led exclusively to the formation of transesterification products

[1]This chapter has been published as **Santos, T. R. d.**, Harnisch, F., and Schröder, U. Electrochemistry for biofuel generation: Transformation of free fatty acids and triglycerides to a - diesel - like (olefin-ether) mixture, ChemSusChem, 8:886-893, 2015.

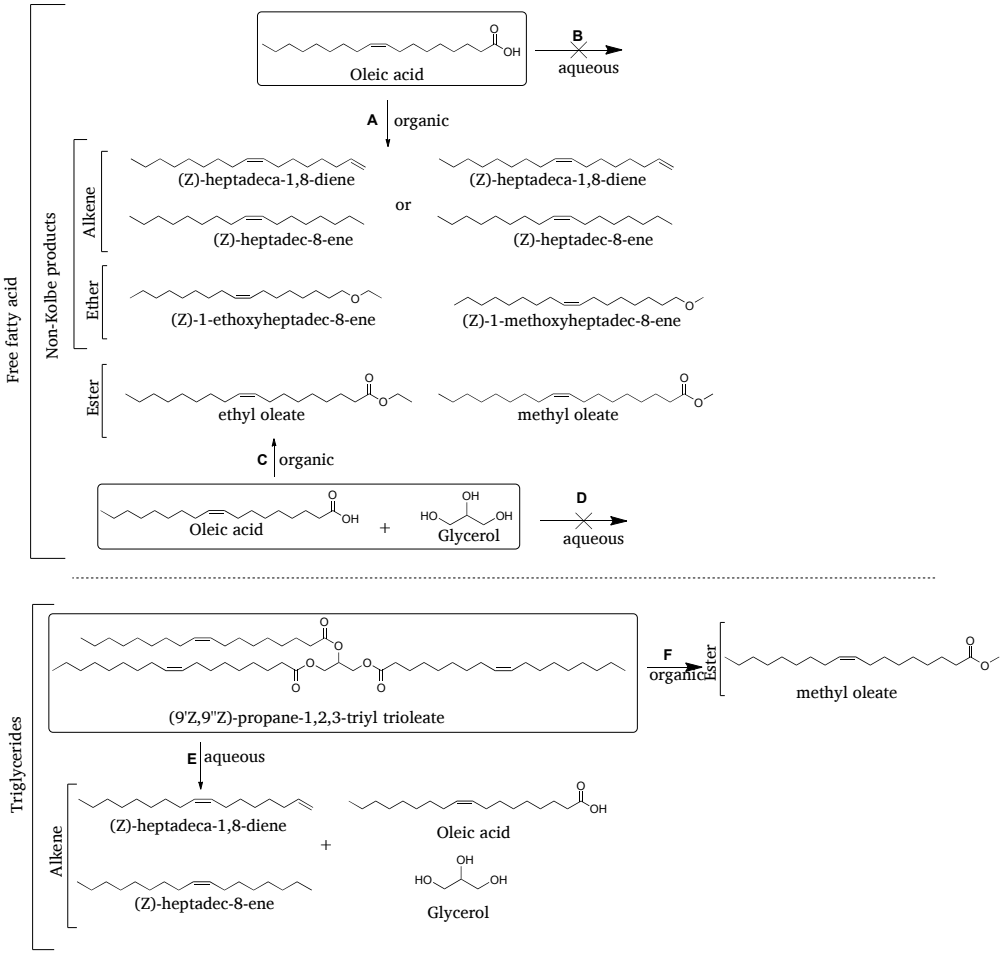

Figure 6.1: Schematic overview of the reaction routes investigated in this work for conversion of free fatty acids, mixture of free fatty acids and glycerin, and triglycerides on the example of oleic acid and triolein. See also Table 6.1 for details.

6.1 Electroorganic Synthesis in Organic Electrolyte Solutions

Kolbe and non-Kolbe reaction are among of the oldest known electroorganic reactions (H. Hofer and Moest 1902; Kolbe 1849). To date, the electrochemical conversion of long-chain carboxylic acid has been demonstrated only for Kolbe reaction, yielding dimer products with a chain lenghts above C_{30} (i.e. paraffins) (Weiper and Schäfer 1990). These compounds possess a boiling point above 450 °C and thus are unsuitable for biofuel applications. The electrochemical transformation of fatty acids via non-Kolbe reaction, yielding C_{15} to C_{20}-alkenes, i.e. olefins, has so far only been reported once, without any detailed information (Busch 2008).

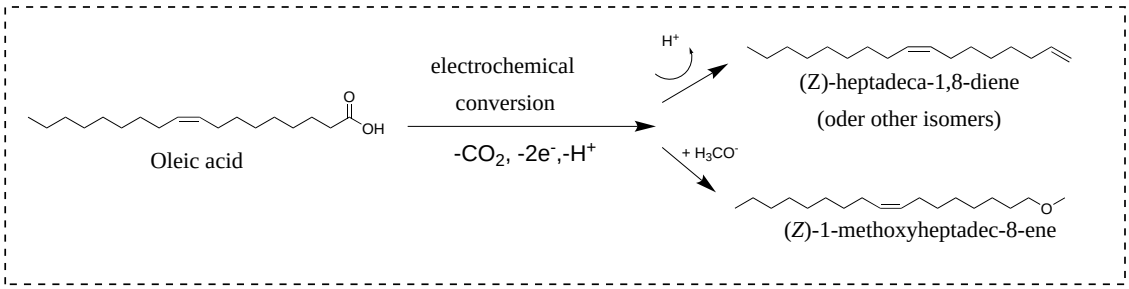

Figure 6.2: Schematic reaction pathways of the electrochemical decarboxylation of oleic acid in organic electrolyte solution

The latter compounds may indeed be suitable for biofuel application, as e.g., the boiling point of heptadecene 300 °C is below that of the boiling range of conventional biodiesel and lies within that of diesel fuel (see Chapter 3). As depicted in Figure 6.1, the electrochemical decarboxylation of fatty acids in alcoholic solution (pathway *A*) leads to a variety of non-Kolbe products comprising alkenes and ethers. Most importantly, the fatty acids are completely electrochemically converted. The product variety can be attributed to the formation of the primary electrochemical decarboxylation product - a carbenium ion - which can either cleave to yield an olefin or react with a nucleophile like an alkoholate to yield and etherFigure 6.2 (Busch 2008) .

From a biofuel perspective the formation of a mixture (that possesses a boiling range rather than a boiling point) may in fact be advantageous, since the combustion process in diesel engines is generally optimized towards a boiling range (see Chapter 3). The gained mixture of ethers and olefins possesses diesel-like qualities: Beside the above mentioned boiling point of heptadecene (see also Table 6.1), the lower heating value H_{LHV} of the gained mixture of around 30 % heptadecane-methyl-ether and 70 % heptadecene is about 42.3 kJ g^{-1} (calculated according to Boie 1957), which exceeds that of FAME-diesel (37 kJ g^{-1}) (F. Lackner et al. 2010)) and is similar to petro-diesel (42.8 kJ g^{-1}) (M. Lackner and Winter 2010)) (see also Chapter 3).

Figure 6.3 shows the detailed results of the electrochemical transformation of oleic acid and stearic acid in ethanolic and methanolic solutions. Thereby Figure 6.3 *A* clearly shows that the conversion of stearic acid and oleic acid is almost complete (> 95 %of conversion) in batch-mode after 4 Farad charge equivalent passed. Certainly, the use of batch-mode operation is not ideal for this reaction type, as at decreasing educt concentration, the impact of side reactions like solvent electrolysis increases and as a consequence the Coulomb efficiency of the decarboxylation decreases. As Figure 6.3 *B* shows for the batch conversion of oleic and stearic acid the CE decreases from 40 % (for 1 F charge equivalent, representing short reaction times) to 20 % for longer reaction times (4 F charge equivalent). As indicated in a previous work from our group (Nilges and Schröder 2013), an increased overall Coulomb efficiency can be expected for a continuous electrolysis process.

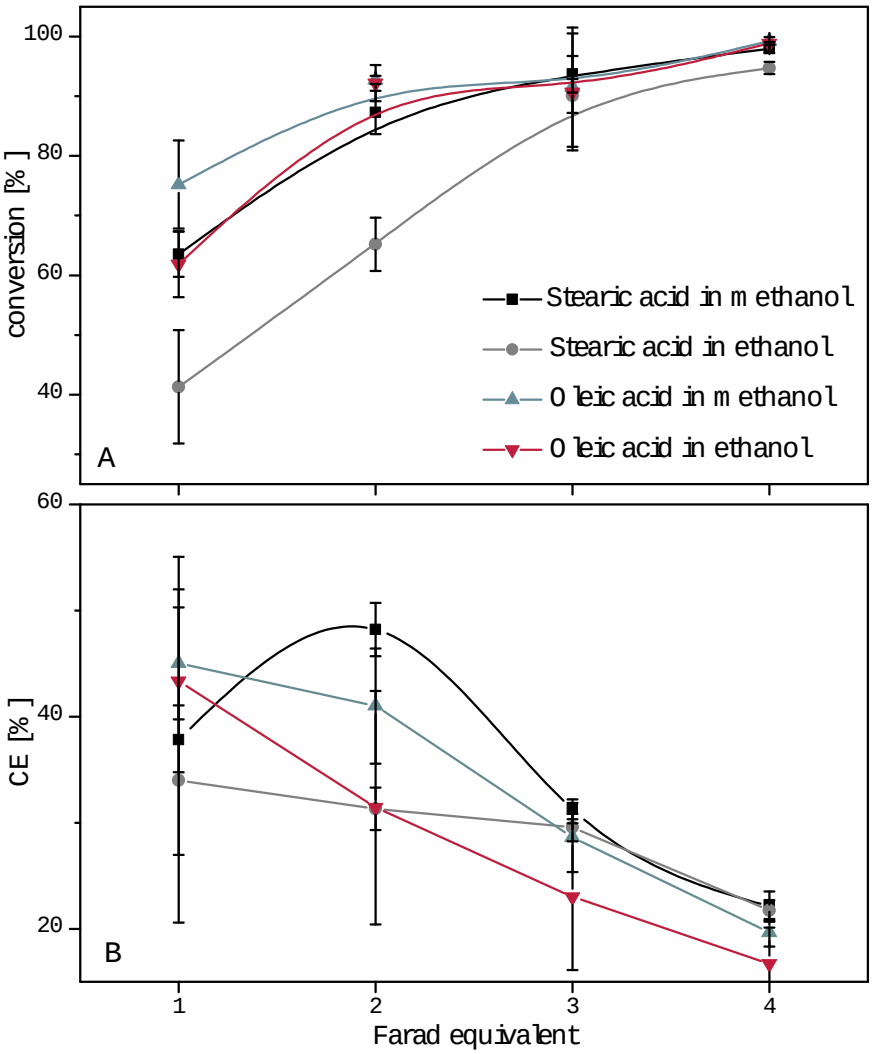

Figure 6.3: Conversion of stearic acid and oleic acid in organic solvents (methanol and ethanol) vs. Farad equivalent B) Coulombic efficiency in terms of educt decomposition

As shown in Figure 6.4, the average selectivity of the combined non-Kolbe products was more than 80 %. The selectivity of ethyl and methyl esters as non-electrochemical side products was 10 % and below. The relative share of the olefin products always exceeds the share of the ethers. For oleic acid as educt the olefin fraction was composed of several isomers including (Z)-heptadec-8-ene, (E)-hepatdec-8-ene, (Z)-heptadeca-1,8-diene, (E)hepatadeca-1,8- diene and hepatadec-1-ene as well as the ether fraction , including e.g. (Z)-17-ethoxyheptadec-8-ene, (E)-17-ethoxyheptadec-8-ene (see Chapter 4.1 for details). Furthermore, no educt specific variations on the product formation were detected and all described fundamental trends were further validated for palmitic acid as starting material (data not shown). Experiments using an educt mixture composed of the free fatty acids and glycerol (Figure 6.1, pathway C)

proofed the trends observed for the pure fatty acids (pathway A).

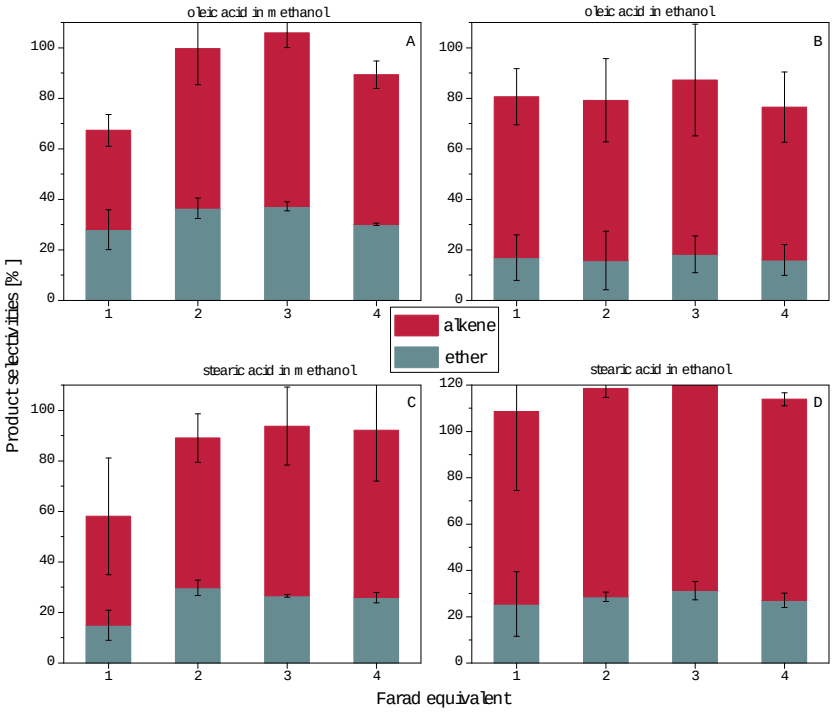

Figure 6.4: Products compositions of the electrochemical decarboxylation of stearic acid and oleic acid in methanol and ethanol as a function of the applied charge equivalent. The electrolyses were performed galvanostatically using a current of 100 mA, corresponding to a current density of 17 mA cm^{-2}: A) Oleic acid in methanol, B) Oleic acid in ethanol, C) Stearic acid in methanol, D) Stearic acid in ethanol.

Since the electrochemical conversion of free fatty acids requires the preceding hydrolysis of a triglyceride (GUNSTONE et al. 2007), it is desirable to develop methods for a direct triglyceride exploitation. For this reason we studied the direct electrochemical conversion of rapeseed oil as an exemplary triglyceride (Figure 6.1, pathway F). Yet, for methanol and ethanol electrolyte solutions these experiments were unsuccessful, as no electrochemical reaction took place and exclusively the transesterification products of the fatty acids with the respective solvent was obtained.

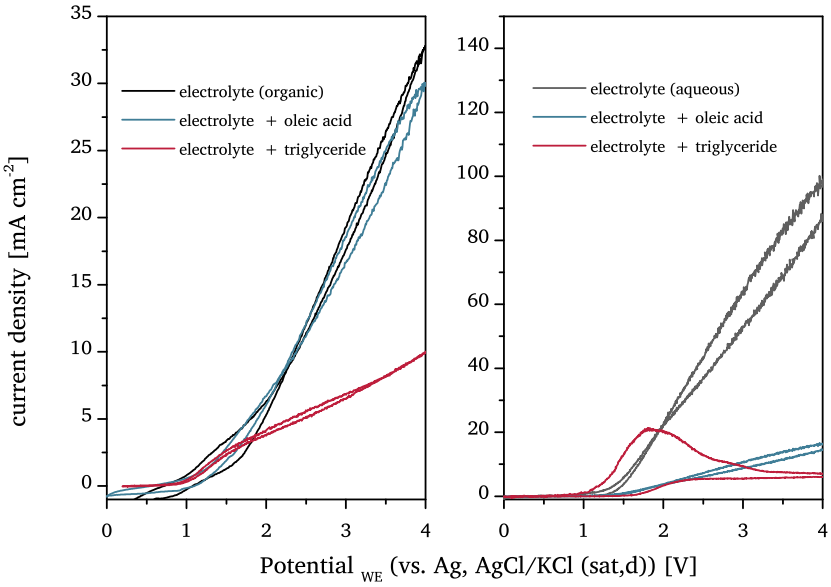

Figure 6.5: Cyclic voltammogramms for the electrochemical oxidation of oleic acid ($0.03\,\mathrm{mol\,l^{-1}}$) and the triglyceride (rapseed oil, $0.01\,\mathrm{mol\,l^{-1}}$), $A)$ in methanolic and $B)$ in aqueous electrolyte solution; $0.03\,\mathrm{mol\,l^{-1}}$ KOH as supporting electrolyte. The voltammograms, recorded at a scan rate of $5\,\mathrm{mV\,s^{-1}}$, show the 2^{nd}. The experiments in aqueous solution were performed with the support of ultrasound

Cyclic voltammetry was performed to gain insights into the mechanistic details of the electrochemical reactions. Figure 6.5 A shows the CVs of the electrochemical decarboxylation of free fatty acids (on the example of oleic acid) and of rapeseed oil in methanolic electrolyte solution. As one can clearly see, the addition of oleic acid does almost not influence the shape of the CV curve. Apparently, the anodic decarboxylation takes place at similar potential as the solvent oxidation. In contrast to the fatty acids, the use of the triglyceride leads to a significant decrease of the oxidation current, indicating a blocking of the electrode surface by triglyceride or reaction products. This finding is in agreement with the above discussion that triglycerides are not electrolyzed and only transesterificated in methanolic solution.

6.2 Electrochemical Decarboxylation in Aqueous Electrolyte

Oils, fats and fatty acids are only sparingly soluble in aqueous solutions. For this reason ultrasound was applied to produce emulsion for electrochemical decarboxylation experiments (Lorimer and P. 2002). Figure 6.5 B shows the, so called, sonoelectrochemical cyclic voltammograms for the electrolyte solution as well for the oleic acid electrolyte emulsion and for rapeseed oil emulsion. The figure illustrates the major difference to the experiments performed in the organic solvents. The addition of the organic substrate to the aqueous

electrolyte solution leads to a significant decrease of the slope of the voltammetric curve due to the suppression of the electrolyte decomposition - the main reaction in the absence of the organic compounds, a phenomenon known for many electroorganic reactions (Beck 1970). The suppression of electrolyte decomposition due to the adsorption of the organic educt allows the electrochemical synthesis to be performed at potentials far more positive (or negative) than the decomposition of the solvent.

The potential of sonoelectrosynthesis was studied using potentiostatic experiments, performed at (3 V vs. Ag/ AgCl) at working electrode. Under these conditions, the strong foam formation of the carboxylate emulsion did not allow to perform successful electrolysis experiments of free fatty acids (pathway *B* and *D*, Figure 6.1). Rapeseed oil (pathway *E*, Figure 6.1), on the other hand, was converted successfully: After 2 Farad equivalents (corresponding to about 2 h a conversion of 50(±1.5) % is achieved with a Coulomb efficiency of 20(±1.5) %. As products, exclusively alkenes were formed (see Figure 6.6).

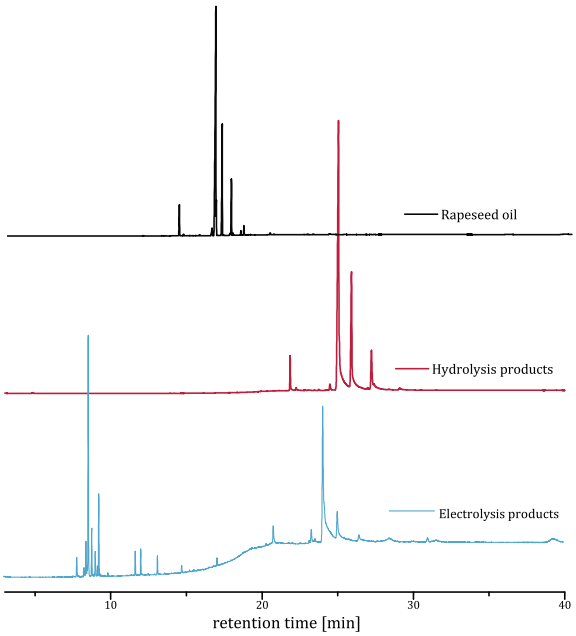

Figure 6.6: GC-FID chromatograms of starting material triglyceride (rapeseed oil, after derivatisation) and electrolysis products

From the standpoint of green chemistry the use of an aqueous electrolyte solution is a clear advantage over organic solvents (P. T. Anastas and Warner 1998), and its advantage can be further supported when comparing of the educt-turnover, $\dot{m}$, in both environments. To achieve an educt turnover rate of, e.g., 0.36 kg m^{-2} h^{-1} in aqueous solutions (at average CE=20 %, j=34 mA cm^{-2}) a cell potential of only ∼ 5 V is needed and the starting materials can be the triglyceride in aqueous solution. In the organic solvent (CE=40 %, j=17 mA cm^{-2}) a cell potential of ∼ 15 V is required and the starting material has to be the fatty acids has to be produced from the triglyceride by hydrolysis beforehand.

Previous sonoelectrosynthetic studies on the oxidation of emulsions of water-immiscible short chain organic acids ($R-CO_2H$) such as hexanoic and heptanoic acid leading to the Kolbe-products $R-R$ hydrocarbons), have been reported by J. D. WADHAWAN et al. 2001. The conversion of long chain carboxylic acids, i.e. fatty acids, and triglycerides via Non-Kolbe sonoelectrosynthesis has been never reported before.

The electrochemical conversion of triglycerides leads to the formation of glycerol as a co-product and diglycerides and monoglycerides as intermediate products. Unfortunately, increasing concentrations of these products during the electrochemical conversion leads to reaction termination, in the present work usually at approx. 50 % of educt conversion. Glycerol is electrochemically active itself, and its electrochemical oxidation in aqueous solutions (mostly at noble metal electrodes), has been reported (KONGJAO et al. 2011; PAGLIARO and ROSSI 2008).

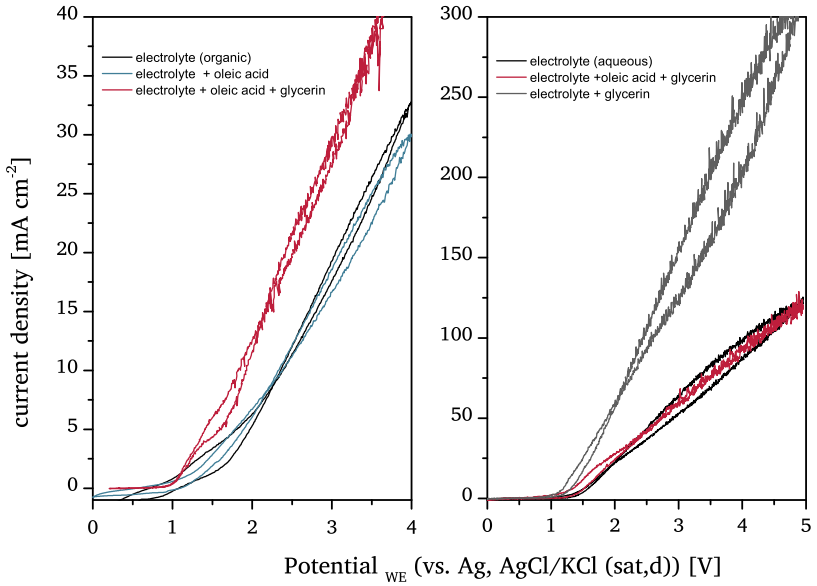

Figure 6.7: Cyclic voltammogramms for the electrochemical oxidation of oleic acid (0.03 mol l^{-1}) and the triglyceride (rapseed oil, 0.01 mol l^{-1})in aqueous electrolyte solution using sono-electrochemistry; graphite working electrodes, 0.03 mol l^{-1} KOH as supporting electrolyte, recorded at a scan rate of 5 mV s^{-1} (always the 2^{nd} scan is shown)

As Figure 6.7 illustrates, its oxidation also takes place at graphite electrodes, seemingly at a lower potential than the oxygen evolution (1 V and 1.4 V vs. Ag/ AgCl, respectively). One may speculate that the glycerol oxidation leads to the formation of reactions products that, for instance, block the electrode surface for the further decarboxylation of the fatty acids (J. WADHAWAN 2001). HPLC-analysis also confirmed the formation of glycerol derived, yet unidentified products. Here, a further understanding of these processes is inevitable to achieve a complete conversion of the starting material.

7 | Energetic Consideration[1]

In order to illustrate the potential economic feasibility of the electroorganic synthesis for the previous described process (see Chapter 5 and 6) an basic energetic assessment was drafted.

7.1 Energy Content of Educts and Products

Table 7.1 shows the energy content of educts and the respective reaction products. When no experimental data were available the method according to Boie, as explained in section 3.2 was used to calculate the lower heating value (H_{LHV}).

Table 7.1: Summary of combustion properties of oleic acidand derivates and levulinic acid and reaction products Afeefy et al. 2011. * Estimated according to Boie Grote and Feldhusen 2005 method using equation 3.2

compound	molecular weight [g mol^{-1}]	H_{LHV} [kJ mol^{-1}]	H_{LHV} [kJ kg^{-1}]
Triolein	885.43	35100	39.64
Oleic acid	282.46	11161	39.51
Methyl Oleate	296.49	11832	39.91
Ethyl oleate	310.51	12525	40.34
Heptadecane	240.47	11351	47.20
Heptadeca-1,8-diene*	236.44	10134	42.86
Heptadec-8-ene*	238.48	10317	43.26
1-methoxyheptadec-8-ene*	268.48	10761	40.08
1-ethoxyheptadec-8-ene*	282.50	11365	40.23
Levulinic acid	885.43	35100	20.8
2,7-octadione	282.46	11161	30.4
3-buten-2-one	296.49	11832	29.5
4-hydroxy-2-butanone	310.51	12525	23.6
n-octane	240.47	11351	44.4
1-butanol	282.50	11365	36.0

[1]This chapter has been published as **Santos, T. R. d.**, Nilges, P., Sauter, W., Harnisch, F., and Schröder, U. Electrochemistry for generation of renewable chemicals: Electrochemical conversion of levulinic acid. RSC Adv., 5:26634-26643, 2015. **Santos, T. R. d.**, Harnisch, F., and Schröder, U. Electrochemistry for biofuel generation: Transformation of free fatty acids and triglycerides to a - diesel - like (olefin-ether) mixture, ChemSusChem, 8:886-893, 2015.

7.2 Energy for the Electrochemical Upgrading Step

The theoretically required electric energy to drive the reaction is defined as the product of the cell voltage (U) and charge (Q): $E_{\text{electric}} = U \times Q$. The molar electric energy, $E_{\text{electric,molar}}$, can be calculated as $E_{\text{electric,molar}} = Z \times z \times F$, with F being the Faraday constant and z being the number of transferred electron per molecule.

Since the reactions of the levulinic acid pathway were performed in half-cell experiments, the energy was calculated here for the respective half-reaction considering the average working electrode potential *vs.* standard hydrogen electrode, SHE as U. For the fatty acids and triglycerides pathway, the experimental cell voltage was applied for calculations.

Thus, the energy consumption in terms of molar energy can be calculated as showed below:

$$E_{\text{EC}} = \frac{z \times F \times U}{CE} (\text{J mol}^{-1}) \tag{7.1}$$

Considering the molar mass of products the specific energy can be calculated. CE is calculated as presented in Chapter 4.2.

$$E_{\text{EC}} = \frac{z \times F \times U}{CE} \times M_{\text{P}} (\text{J kg}^{-1}) \tag{7.2}$$

Energy Storage Efficiency

In order to assess the energy efficiency of the reactions shown in Figure 5.1, a calculation of the ”energy storage efficiency” (ESE) is necessary, it is defined as:

$$E_{\text{storage efficiency}} = \frac{\Delta H_{\text{LHV}}}{E_{\text{EC}}} \times 100(\%) \tag{7.3}$$

7.3 Energetic Considerations for Electrochemical Levulinic acid Conversions

Alternatively to their exploitation as platform chemicals (see Table 2.1) the electrochemical conversion of LA can be used for the storage of electric energy. The derived products may serve also as alternative ”green” fuels for combustion engines. To be exploited as an alternative fuel at least two key properties of a chemical have to be considered (see 3: (i) its ignition properties and (ii) its calorific value. Both properties are strongly influenced by the oxygen content of a substance. Dependent on the nature of the functional group, oxygen can be removed either reductively (*via* electrocatalytic hydration), or oxidatively (e.g., *via*

Kolbe reaction). Certainly, a reduction may represent a direct way to store electric energy into a chemical compound, whereas a (partial) oxidation lowers the absolute energy content with respect to the educt/starting material. Yet, the electrochemical oxidation reaction of levulinic acid (and its primary products) not only allows removing functional groups like carboxylic groups from a given product (thus improving its ignition properties), but it also allows increasing the mass related energy density of the product by removing the oxygen containing functional groups. For instance the energy density of levulinic acid — a compound that is not suitable to be used in combustion engines due to the carboxylic group — $H_{\mathrm{LHV}} = 20.8\,\mathrm{MJ\,kg^{-1}}$ can be increased to that of 1-butanol ($H_{\mathrm{LHV}} = 36\,\mathrm{MJ\,kg^{-1}}$) and of n-octane ($H_{\mathrm{LHV}} = 44.4\,\mathrm{MJ\,kg^{-1}}$) by electrochemical oxidation (see Table 7.1). For the determination of the respective lower heating value, H_{LHV}, the method according to Boie was used (see 3 for details).

In order to assess the energy efficiency of the reactions shown in Figure 5.1, a calculation of the "energy storage efficiency", *i.e* the difference of the lower heating values of the educt and product divided by the energy needed for the electrochemical reaction, for the different compounds and the input energy for the reaction is present in Table 7.2. Thereby the theoretical and experimentally electric energy required to drive the reaction(s) was compared to the increase in terms of energy density of the products molecules. Since in this study all reactions were performed in half-cell experiments, the energy calculation was based on the respective half-reaction, considering the needed average working electrode potential (*vs.* standard hydrogen electrode, SHE). The average working electrode potential for the reduction was -1.8 or $-1.5\,\mathrm{V}$ (*vs.* Ag/AgCl, corresponding respectively to a potential of -1.5 and $-1.3\,\mathrm{V}$ *vs* standard hydrogen electrode, SHE). For the oxidation reactions the applied working electrode potential varied from 2 or 10 V (*vs.* Ag/AgCl, corresponding respectively to a potential of 2.2 and 10.2 V *vs* standard hydrogen electrode, SHE), please note that the higher oxidation potentials were only applied for systems using organic solvents.

Table 7.2 shows the so far maximum achieved energy storage efficiencies, Regarding the one step reactions, only the reductions provide the possibility for energy storage. Most of the reduction exhibit a potential for energy storage efficiency higher than 70 %. Here, for the theoretically most favorable reduction of levulinic acid into γ-valerolactone, (with a maximum energy storage efficiency of 92 %), only 16 % are achieved in the present study (due to the lower achieved CE from 20 %). However, clearly closer matches of the theoretical and achieved energy storage capacity are shown, *e.g.* for route II and route IX. For the two-step reactions the theoretical maximum values are lower and the achieved energy storage efficiencies are maximum ca. 10 % (route II combined with route VII). These calculations show that electrochemical conversion, here of levulinic acid and it primary products, can provide an interesting and potentially energetically and thus economically competitive alternative not only for chemical production, but also for fuel generation and energy storage.

Table 7.2: Estimation of the energy storage efficiency based on heating values and the molar electric energy for reduction conversions and combination of the two step reactions (details to reaction pathways at Figure 5.1)

							achieved[b]				theoretical maximum			
	route	product → educt	$H^a_{LHV_{educt}}$	$H^a_{LHV_{product}}$	ΔH_{LHV}	z[c]	E_{WE}	CE	molar electric energy	ESE	E_{WE}	CE	molar electric energy	ESE
			kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}		*V*	%	kJ mol^{-1}	%	V	%	kJ mol^{-1}	%
reduction	*I*	levulinic acid → γ-valerolactone	2420	2650	230	2	-1.5	20	1447	16	-1.3	100	251	92
	II	levulinic acid → valeric acid	2420	2840	420	4	-1.5	60	965	44	-1.3	100	502	84
	VI	levulinic acid → 2-methyl-THF	2650	2863	213	4	–	–	–	–	-1.3	100	502	42
	VIII	2,7-octanedione → n-octane	4323	5047	724	8	-1.5	10	10526	7	-1.3	100	1003	72
	IX	4-hydroxy-2-butanone → 1-butanol	2083	2446	363	4	-1.3	58	865	42	-1.3	100	502	72
	X	4-hydroxy-2-butanone → 1,3-butanediol	2083	2273	190	2	-1.3	2	12543	2	-1.3	100	251	76
oxidation	*III*	levulinic acid → 2,7-octanedione	2420	4323	-517	1	5.2	90	545	-95	2.5	100	241	-214
	IV	levulinic acid → 4-hydroxy-2-butanone	2420	2083	-337	2	2.7	10	10420	-3	2.5	100	482	-70
	V	γ-valerolactone → 3-buten-2-one	2420	2067	-353	2	2.7	20	2171	-16	2.5	100	482	22
	VII	valeric acid → n-octane	2840	5047	-633	1	3.7	40	830	-76	2.5	100	241	-262
two steps	*I+VI*	levulinic acid → 2-methyl-THF	2420	2863	443		–	–	–		–	100	753	59
	II+VII	levulinic acid → n-octane	2420	5047	207				1795	12		100	743	28
	III+VIII	levulinic acid → n-octane	2420	5047	207				11071	2		100	1245	17
	IV+IX	levulinic acid → 1-butanol	2420	2446	26				11285	0		100	984	3
	IV+X	levulinic acid → 1,3-butanediol	2420	2273	-147				22963			100	733	-20

[a] estimated according to Boie and data for levulinic acid, valeric acid and γ-valerolactone from Xin et al. 2013 , [b] achieved in this study, [c] number of electrons

7.4 Energetic Considerations for Electrochemical Conversion of Fatty acids and Triglycerides

Calculation of Educt Conversion Rate

To assume the production rate, the conversion rate, $\dot{m}$, of the starting material was calculated, considering oleic acid (M= 282 g mol^{-1}) as educt and a two electron ($z = 2$) reaction. The decarboxylation of oleic acid by use of Non-Kolbe electrolysis undergoes a $1 : 2$ stoichiometry conversion, i.e. each molecule of oleic acid consumes two electrons (z=2). The current density, j, was 17 mA cm^{-2} in organic electrolyte solutions and 34 mA cm^{-2} in aqueous electrolyte solutions.

$$\dot{m} = \frac{j \times CE \times M}{z \times F} \tag{7.4}$$

Table 7.3: Conversion rates for the pathways A and E (see Chapter 6), showing the values for the average experimentally achieved and theoretical maximum CE values

		CE [%]	$\dot{m}$ [mg cm^{-2} h^{-1}]
Pathway A	Experimentally	50	36
	Theoretical max.	100	90
Pathway E	Experimentally	20	36
	Theoretical max.	100	179

Calculation of the Energy Input for Biomass Processing

Figure 7.1 illustrates the main workflow for the generation of biofuel from triglycerides. All methods share a common energy input for agriculture, transportation, extraction and refining of 12.5 kJ g^{-1} (Kaltschmitt 2009). The obtained vegetable oil than can either be used directly for combustions engines (Knothe 2011) or is further processed in order to improve its combustion quality. The theoretical yield of free acid from the hydrolysis of glycerol trioleate is close to 96 % (Gunstone et al. 2007). 7.2 allows the determination of energetic consumption for an electrochemical upgrading. Here the energy need for FAME-biodiesel (further 4.3 kJ g^{-1}) and green-diesel (3.9 kJ g^{-1}) production are well known (Serrano-Ruiz et al. 2012). These may now serves as benchmarks for comparison with the electrochemical pathway.

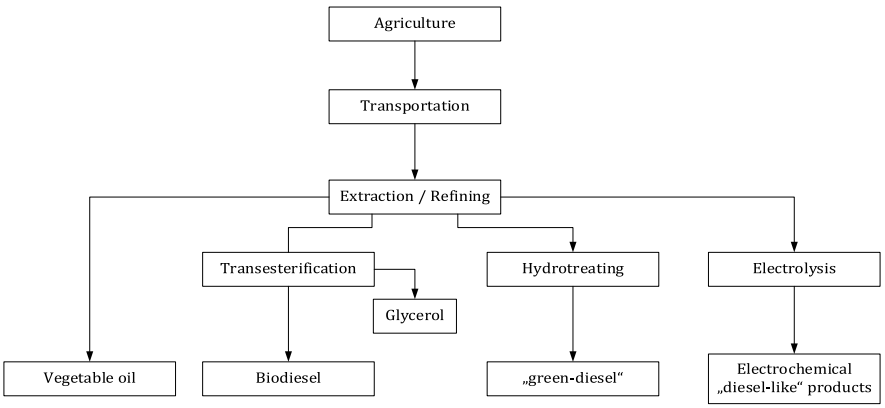

Figure 7.1: Flowchart of the generation of biofuel from triglyceride based biomass.

Assessment of the Energetic Efficiency of the Overall Process

Based on Figure 7.1 and Table 7.1 it is possible to estimate the Net Energy Value (NEV) (Bureau et al. 2010):

$$\mathrm{NEV} = \mathrm{Energy}_{\mathrm{output}} - \mathrm{Energy}_{\mathrm{input}} \tag{7.5}$$

Figure 7.2 shows how the net energy value varies with the cell potential and the Coulombic efficiency. The higher the applied cell voltage the higher the specific energy input in the electrochemical system, decreasing thereby the efficiency of the process. The Net Energy Ratio (NER) 7.6 also can be used to estimate the efficiency of the process and are calculated as shown below.

$$\mathrm{NER} = \frac{\text{Returned units of energy}}{\text{Unit of consumed energy}} \tag{7.6}$$

The main results are summarized in Table 7.4, from which one can clearly deduce that the electrochemical processing of fats and oils — although being in their infancy and needing to overcome technological hurdles — provide an interesting and potentially energetically and thus economically competitive alternative when compared to conventional production routes. Further the products of the electrochemical conversion of fatty acids are expected to present better combustion properties in comparison with biodiesel.

Table 7.4: Energetic balance for electrochemical biofuel generation from triglycerides compared with the transesterification and hydrotreating process.

method		products	energy input [MJ kg^{-1}]	fuel energy output [MJ kg^{-1}]	NER
Biodiesel production		Fatty acid methyl-esters	17	37	2.2
Hydrotreating		Alkanes	16	43	2.6
Electroorganic	5V (Pathway *E*)	Alkenes	18	42	2.3
synthesis	15V (Pathway *A*)	Alkenes/ ethers (70 : 30)	28	42	1.49

The decisive feature that determines the energy efficiency (and the net energy ratio) of an electrochemical process is the used cell voltage of the electrochemical cell during the electrolysis process. For the used system, the average cell voltage (U) ranged from 3 V (for the aqueous electrolyte solutions) to a maximum of 42 V for the ethanolic and methanolic electrolyte solutions. This illustrates the advantage of using aqueous electrolyte solutions rather than the organic solvents.

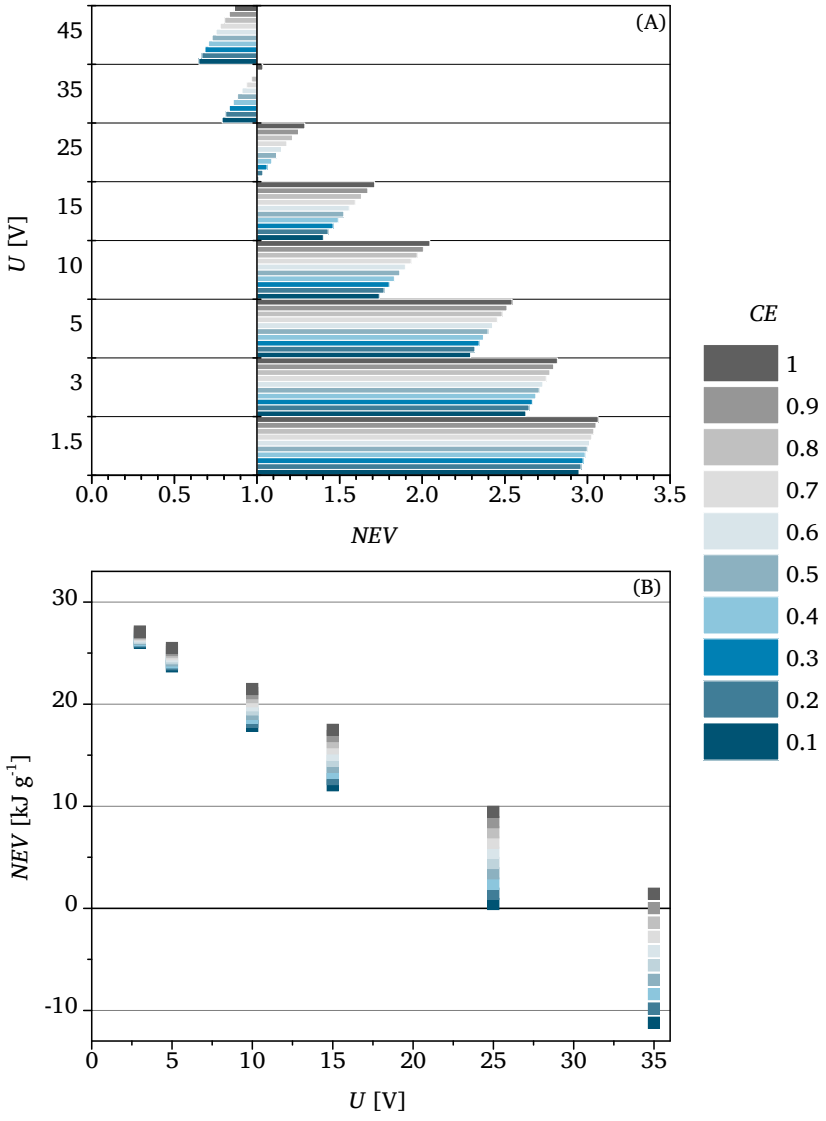

Figure 7.2: Net energy value and net energy ratio of the electrochemical upgrading as function of cell voltage (U) and Coulombic efficiency (CE)

8 | Summary and Outlook

The integration of biorefinery products into existing petroleum-derived compounds and processes requires new approaches to overcome differences in terms of feedstock, conversion processes and products. The idea of the present work was to provide a new perspective for the use of electroorganic synthesis in the conversion of biomass derived compounds into chemicals and alternative fuels. A first estimation of the potential of reactions products as a alternative fuel was made by a conceptual evaluation of combustion properties like cetane number and calorific value which confirms the suitability of some reaction products as alternative fuel. The experimental results illustrate the effective application of electroorganic syntheses for selective conversion of levulinic acid via one or two steps reaction to products like valeric acid, γ-valerolactone, 2,7-octandione, 4-hydroxy-2-butanol and n-octane. In addition, this work reports the electrochemical conversion of triglycerides into diesel-like olefin/ether mixtures and olefins. Additionally, a preliminary energetic assessment of the presented electroorganic synthesis routes and their comparison to existing processes provides further evidence of its technological and economic potential.

There are several concepts, tools and methods for the evaluation of combustion engine related properties of potential (bio)fuel molecules, but there is a great difficulty to implement petro-diesel derived protocols for testing prospective (bio)fuel molecules. This was an impulse to the performed basic theoretical assessment of biomass derived chemicals in the light of their prospective application as fuel in order to allow the directions of research activities in a early stage. Using a theoretical approach has clearly some limitations, but since experimental data are very limited, reliable models for the estimation of fuel and combustion properties are indispensable for the development of alternative fuels. The energy content is one of the parameters that was estimated. It is one important criterion to evaluate the use of a compound as a potential fuel and it is particularly relevant in the context of the present work. Among others, this value is necessary for the evaluation of the energy efficiency of the electrochemical upgrading reactions. An exemplary calculation of the H_{LHV} using two different methods (Dulong and Boie) as an function of the experimental value shows a better fitting using the Boie algorithm. The deviation for compounds like n-octane and n-heptadecane is about 1 %, providing a good alternative for the first energetic estimation shown in Chapter 7.

Chapter 5 presented an approach for primary and secondary conversion of levulinic acid by means of electrochemical oxidation and reduction. The results introduce a new portfolio of chemicals that can be obtained via electrochemical conversion of LA, including: valeric acid, n-octane, γ-valerolactone, 2,7-octadione, 4 hydroxy-2-butanone and 3-buten-2-one as well as 1-butanol, 1,3-butanediol. As shown in Table 2.1, gVL and VA are both important intermediates for the chemical industry and gVL has even been proposed to be used directly as solvent. The results presented in Section 5.1 reinforce the usefulness of the concept of electroorganic synthesis as an alternative for the primary conversion of levulinic acid.

Since downstream processes represent a considerable share of the costs in a chemical process, the spontaneous separation of valeric acid in reactions at high start concentrations of levulinic acid shows a clear advantage of the electrochemical reduction in aqueous solution over conventional techniques. At the current stage of research the most remarkable limitation of this reaction pathway is due to the fact that gVL has always been formed as by-product with an average of about 15 % of the total products. Further experimental investigation need to be carried out to establish whether is it possible to minimize this by-products formation. An alternative could be working in a continuous system as presented by Xin et al. 2013 and in section 4.2. Another alternative to increase the selectivity could be tailoring the electrode material or the electrolyte solution, which have also been tested in the present work. Unfortunately, for the reaction leading to valeric acid it was not possible to find a better electrode/electrolyte combination that minimizes the share of by-products under the applied conditions. On the other hand, the conversion of levulinic acid to gVL was successful at three different electrodes and in all cases no valeric acid was detected as by-product. The Coulombic efficiency for these reactions was not higher than 20 % and has to be improved for application in lager scale. Preliminary work indicates, that the reactions at low temperature could have a positive effect in improving the Coulombic efficiency. However this effect is quite specific and has to be investigated in detail in each case, since e.g. the adsorption and desorption influences directly the electrocatalytic hydrogenation and this interaction depends of electrode, electrolyte and educt.

The electrochemical oxidation of levulinic acid and derived products for different reaction pathways was also explored as shown in Figure 5.1. Both, one and two electron oxidation processes have been investigated. Although the performance of the reactions aiming a two electron oxidation of both levulinic acid and its reaction product valeric acid was not ideal, since a selective formation of the desired products was very limited, this study highlighted the complexity of the involved reactions. It illustrates that not all assumptions for electrolysis in organic solvents can be easily transfered for aqueous systems. The non-Kolbe reaction of valeric acid, for example, shows a successive decomposition (along the C-chain) of the formed products. The application of the most favorable reactions conditions as described in the literature for similar reactions in organic solvents did not lead to the expected results. First experiments conducted in a flow system result in slight improvements, but a

decrease in the formation of by-products was not as high as expected. The two-electron oxidation pathway reactions of levulinic acid have also been demonstrated in the present work, but unfortunately the results are still inconclusive and considering the promising results achieved for the subsequent reaction of 4-hydroxy-2-butanone the improvement of selectivities should be addressed by further studies. As preliminary investigations have shown the possibility of ether formation when working in ethanol and methanol as shown in Chapter 6 for the long chain fatty acids could also be an interesting approach depending on the intended final application.

The Kolbe electrolysis (one-electron decarboxylation) of carboxylic acids in organic solvents is well described in the literature, but only special cases, as for example butyric acid, have been investigated in detail in aqueous systems. The results obtained for the electrochemical decarboxylation of valeric acid (derived from levulinic acid) provides additional support for the application of electroorganic synthesis using water as solvent. Once again it provides the spontaneous separation of formed products as further advantage. As aforementioned, the reactions in aqueous electrolyte solution still demand further investigations, since the reaction mechanisms and kinetics are not the same as in the organic system, which could not be satisfactorily clarified within the scope of the present work. Especially the influence of the carbocation seems to play a decisive role in this context since the formation of esters is more pronounced but the proposed reaction mechanism could not be yet proven.

Further, Chapter 6 demonstrates that fatty acids and triglycerides can be electrochemically converted into of diesel-like olefin/ether mixtures, which can potentially be applied as biofuels. Even more promising is the direct transformation of triglycerides into alkenes in aqueous electrolyte solutions using sonoelectrochemical decarboxylation. Noteworthy, these electroorganic syntheses are performed obeying important rules of green chemistry. As fats and oils are already exploited for biofuel generation the agricultural as well as technological infrastructure already exist making the integration of electroorganic syntheses more feasible. Nevertheless, this research has raised many questions needing of further investigation. Regarding the reactions in organic electrolyte solution, future work should focus on understanding the reaction mechanism leading to the formation of the main products olefin and ethers in order to find a way to shift and increase the product selectivity in both directions. The minimization of by-products formation, in this case the methyl and ethyl esters, has also to be addressed avoiding the need of further separation steps, in the case where the ester fraction in the final mixture is higher than acceptable. Future studies on the direct conversion of triglycerides in organic solvents are therefore required in order to better evaluate the potential of this reaction. This is os special interest because the experiments with free fatty acids and glycerol, simulating a complete hydrolysis of a triglyceride, have not shown any restriction as occurs in aqueous system. The prospect of being able to directly convert triglyceride using water as solvent should serve as an incentive for further work in this field. For this purpose subsequent research should deal with two main issues, foam formation for reac-

tions using only free fatty acids and the interruption of the decarboxylation reaction when triglycerides are applied as educt. In the case of foam formation, an alternative could be the application of anti-foaming agents as for example oils, alcohols or glycols, considering at least the following points: electrochemical inertness at the applied conditions, emulsion stability, easy separation from products and reusability. An even more important matter to be solved is the interruption of the decarboxylation if glycerol is present in the aqueous system probably due to concurrent reactions at the anode surface. This issue could be addressed in two different ways: by finding an alternative anode, where the decarboxylation is preferred and glycerol do not react or by using and adsorber for removing soluble glycerol. According to Yori et al. 2007 a cyclic operation of fixed beds of silica gel can be applied as a simple and feasible alternative to the conventional "wet" methods deglycerolization.

In Chapter 7 energetic considerations regarding the electroorganic synthesis and its potential as energy storage method are presented. Considering the use of electrochemistry for the production of liquid fuels (also described as electrofuels), a first energetic assessment of electroorganic syntheses for the conversion of long chain fatty acids compared to existing catalytic routes, like transesterification and hydrotreating shows the potential of investigated technology and may serve as impulse for further research in this field. Apart of the energetic evaluation the economic viability will also play an import rule for the establishment of new technologies, so it can be expected, that the development in this area is also strongly dependent of variations in crude oil price and political interest. At the current stage of development and with the achieved results it is not possible to state any prediction in this direction. Further, the use of electrochemical synthesis and upgrading pathways, specially the reductive reactions as presented in Chapter 5, may play an important role for the storage of unused energy during overproduction, since renewable energies like wind power and solar energy are characterized by a fluctuating electricity production. Here the main challenge is the development of suitable reactors systems in order to achieve a better reaction control and maximal Coulombic efficiency. In order to achieve maximal efficiency and enable the implementation of this technology in large scale further research in both, fundamentals of the different reactions and engineering of the entire process will be essential.

A | Appendix

A.1 Raw Data for Calculations of Properties of Prospective Biofuels

Table A.1: Raw data of Figure 3.2, [a](Arcoumanis et al. 2008; Bertola and Boulouchos 2000; Song et al. 2000; *title* 2012; Yanowitz et al. 2011), [b](Mani Natarajan et al. 2001; Song et al. 2000)

Substances	Auto ignition temperature [a] / °C	Cetane Number [b] / [-]
Hydrocarbons		
Dodecane	200	87
n-Tridecane	202	90
n-Pentadecane	202	96
n-Hexadecane	202	100
heptadecane	202	105
n-Heptane	204	56
n-Nonane	205	72
n-Decane	208	77
n-Octane	210	64
n-Tetradecane	220	95
n-Hexane	224	45
1-tetradecene	235	79
1-nonene	237	51
1-undecene	237	65
Undecane	240	81
1-hexadecene	240	88
cyclohexane	245	13
bicyclohexyl	245	53
n-butylcyclohexane	246	47
1-octene	250	41
1-octadecene	250	90
trans-decalin	255	48
methylcyclohexane	260	20
1-heptene	260	32
1-hexene	265	27
n-Pentane	285	30
cyclooctane	290	22
3-methylpentane	300	30
2,3-dimethylpentane	337	21
2,4-dimethylpentane	337	29
1-n-butylnaphthalene	360	6
2,2-dimethylbutane	405	24
sec-butylbenzene	415	6
2,4,4-trimethyl-1-pentene	420	10
ethyl benzene	430	8
1,3-diethylbenzene	450	9
Isohexadecane	472	15
1,2-diphenylethane	480	1
diphenylmethane	485	11
1,3-dimethylbenzene	525	1
1-Methylnaphthalene	529	0

biphenyl	570	21
alcohols		
1-octadecanol	230	81
1-hexadecanol	235	68
1-tetradecanol	240	51
1-decanol	255	50.3
1-octanol	270	39.1
2-ethyl-1-hexanol	270	23.4
1-heptanol	275	28
1-dodecanol	275	63.6
1-nonanol	277	46.2
1-undecanol	277	53.2
1-hexanol	284.9	23.3
1-pentanol	300	20
1-butanol	342.9	17
1-propanol	371	12
sec-butanol	405	13.5
iso-Butanol	415	15
Ethanol	420	10
Methanol	463	3
tert-butanol	478	15.5
acids and ester		
oleic acid	363	46.1
decanoic acid	377	47.6
2-Ethoxyethyl acetate	379	40
ethyl levulinate	425	5
Dimethyl carbonate	458	35
ether		
diethyl ether	160	160
dipentyl ether	171	111
2-ethoxyethyl ether	174	113
dibutyl ether	185	91
Diethylene glycol dimethyl ether	190	112
Triethylene glycol dimethyl ether	195	120.0 [8]
1.2-dimethoxyethane	200	90
dipropylene glycol monomethyl ether	205	42
Dipropylene glycol monomethyl ether	205	42
triethylene glycol monomethyl ether	210	75
2.5.7.10-tetraoxaundecane	210	115
butylal	220	74
dimethyl ether	235	55
dimethoxymethane	235	50
2-butoxyethanol	238	35
Dioxolane	274	30
tripropylene glycol monomethyl ether	277	63
2-methoxyethanol	286	13
1-methoxy-2 propanol	287	19
furanics		
2-Methyltetrahydrofuran	270	23.5
2-methylfuran	450	17
aldehydes and ketones		
octanal	190	80.5
3-octanone	330	35.2
2-heptanone	393	30

Table A.2: Raw data of Figure 3.3, [a](Afeefy et al. 2011), [b](Mollenhauer and Tschöke 2007; Song et al. 2000)

Substance	H_f [a] / kJ mol^{-1}	**Cetane Number**[b] / [-]
hydrocarbons		
heptadecane	-393.9	105
n-Hexadecane	-374.8	100
n-Pentadecane	-354.8	96
n-Tetradecane	-332.1	95
n-Tridecane	-311.5	90
Dodecane	-289.4	87
Undecane	-270.8	81
n-Decane	-249.5	77

1-hexadecene	-248.4	88
n-Nonane	-228.2	72
bicyclohexyl	-215.7	53
n-butylcyclohexane	-213.7	46.5
1,3,5-trimethylcyclohexane	-212.1	30.5
n-Octane	-208.5	64
2,4-dimethylpentane	-201.6	29
2,3-dimethylpentane	-198.7	21
n-Heptane	-187.6	56
2,2-dimethylbutane	-185.9	24.4
trans-decalin	-182.1	48
3-methylpentane	-171.9	30
n-Hexane	-166.9	45
methylcyclohexane	-154.7	20
n-Pentane	-146.9	30
cyclohexane	-123.4	13
2,4,4-trimethyl-1-pentene	-110.5	10
1-octene	-81.3	41
1-heptene	-62.3	32
1-hexene	-43.5	27
sec-butylbenzene	-18.4	6
1,3-dimethylbenzene	17.3	1
ethyl benzene	29.9	8
1-Methylnaphthalene	116.9	0
diphenylmethane	139	11
1,2-diphenylethane	142.9	1
biphenyl	181.4	21
ethers		
Diethylene glycol dimethyl ether	-521.3	112
butylal	-501	74
dipentyl ether	-390	111
2-methoxyethanol	-376.9	13
dimethoxymethane	-348.5	50
1.2-dimethoxyethane	-342.8	90
dibutyl ether	-332.8	91
Dioxolane	-298	30
diethyl ether	-252.1	160
dimethyl ether	-184.1	55
alcohols		
1-hexadecanol	-517	68
1-tetradecanol	-474.8	51
1-dodecanol	-436.6	63.6
1-decanol	-396.6	50.3
1-nonanol	-376.5	46.2
2-ethyl-1-hexanol	-365.3	23.4
1-octanol	-355.6	39.1
1-heptanol	-336.5	28
1-hexanol	-315.9	23.3
tert-butanol	-312.5	15.5
1-pentanol	-294.6	20
sec-butanol	-292.8	13.5
iso-Butanol	-283.8	15
1-butanol	-274.9	17
1-propanol	-255.1	12
ethanol	-234.8	10
methanol	-201	3
acids and ester		
tristearin	-2199	85
tripalmitin	-2075	89
triolein	-1843	45
trilaurin	-1828	100
diethyl adipate	-891.6	15
isobutyl stearate	-827.2	99.3
dibutyl maleate	-821.7	26.5
butyl stearate	-818	80.1
propyl stearate	-797.5	69.9
methyl arachidate	-784.1	100
decyl caprate	-776.6	81
butyl palmitate	-776.6	87
ethyl stearate	-776.6	86
octadecyl acetate	-775.7	90
isopropyl palmitate	-774.5	82.6
methyl stearate	-743.1	81
ethyl palmitate	-735.5	80
hexadecyl acetate	-734.3	86
methyl palmitate	-701.7	74.5
butyl oleate	-699.1	61.6
ethyl myristate	-694.5	66.9

propyl laurate	-673.6	71
methyl myristate	-660.7	66.2
ethyl oleate	-658.1	53.9
ethyl laurate	-653.1	73
acetic acid. dodecyl ester	-651.9	77
isopropyl decanoate	-651	46.6
oleic acid	-644.3	46.1
propyl decanoate	-632.6	52.9
octyl valerate	-632.6	49
methyl oleate	-624.3	55
ethyl levulinate	-620.9	5
methyl laurate	-619.2	61.4
butyl octanoate	-612.1	39.6
ethyl decanoate	-612.1	51.2
decyl acetate	-610.9	62
2-Ethoxyethyl acetate	-610	40
decanoic acid	-598.3	47.6
methyl decanoate	-578.2	47.2
ethyl octanoate	-570.7	42.2
Dimethyl carbonate	-569.9	35
linoleic acid. ethyl ester	-538.1	37.1
methyl octanoate	-536.8	33.6
butyl butanoate	-529.7	17.8
linoleic acid	-524.3	31.4
methyl heptanoate	-516.3	33.5
methyl linoleate	-504.2	42.2
methyl caproate	-495.8	24
linolenic acid	-405	20.4
linolenic acid. methyl ester	-385	22.7
methyl sorbate	-286	6
ether		
Diethylene glycol dimethyl ether	-521.3	112
Butylal	-501	74
dipentyl ether	-390	111
2-methoxyethanol	-376.9	13
dimethoxymethane	-348.5	50
1.2-dimethoxyethane	-342.8	90
dibutyl ether	-332.8	91
Dioxolane	-298	30
diethyl ether	-252.1	160
dimethyl ether	-184.1	55
furanics		
2-Methyltetrahydrofuran	-225	23.5
2-methylfuran	-76.4	17
Aldehydes and ketones		
3-octanone	-322	35.2
2-heptanone	-300	30
octanal	-289	80.5

Table A.3: Raw data of Figure 3.4

substances	H_{LHV} / kJ g^{-1}	$\boldsymbol{H}_{LHV}$(Dulong) / kJ g^{-1}	H_{LHV} (Boie) / kJ g^{-1}
hydrocarbons			
1-Methylnaphthalene	39.38	40.13	39.02
cyclooctane	39.5	42.23	40.44
diphenylmethane	39.61	40.22	39.08
Benzol	40.19	40.7	39.4
Tetralin	40.58	41.93	40.24
Toluol	40.58	41.58	40
1,3-dimethylbenzene	40.86	42.23	40.44
ethyl benzene	40.98	42.23	40.44
1,3-diethylbenzene	41.45	43.13	41.04
sec-butylbenzene	41.5	43.13	41.04
trans-decalin	42.62	45.41	42.58
bicyclohexyl	42.83	45.59	42.71
methylcyclohexane	43.45	46.5	43.32
n-butylcyclohexane	43.51	46.5	43.32
cyclohexane	43.53	46.5	43.32

1-hexadecene	43.92	46.5	43.32
heptadecane	44.02	47.13	43.74
n-Hexadecane	44.04	47.17	43.77
n-Pentadecane	44.08	47.21	43.8
2,4,4-trimethyl-1-pentene	44.08	46.5	43.32
n-Tetradecane	44.11	47.26	43.83
n-Tridecane	44.16	47.32	43.87
2-octene	44.17	46.5	43.32
Dodecane	44.21	47.39	43.92
Undecane	44.26	47.47	43.97
2,2,5-trimethylhexane	44.28	47.68	44.11
1-octene	44.3	46.5	43.32
n-Decane	44.33	47.56	44.03
1-heptene	44.39	46.5	43.32
n-Nonane	44.42	47.68	44.11
1-hexene	44.5	46.5	43.32
n-Octane	44.52	47.82	44.21
2,4-dimethylpentane	44.56	48.01	44.34
2,3-dimethylpentane	44.57	48.01	44.34
n-Heptane	44.66	48.01	44.34
2,2-dimethylbutane	44.66	48.25	44.5
3-methylpentane	44.8	48.25	44.5
n-Hexane	44.84	48.25	44.5
n-Pentane	45.08	48.59	44.73
alcohols			
Glycerol	16.06	16	16.22
Ethylene glycol	16.98	17.14	17.06
methanol	19.95	20.42	19.47
ethanol	26.86	28.36	26.73
1-propanol	30.77	32.59	30.61
tert-butanol	32.77	35.23	33.01
sec-butanol	32.99	35.23	33.01
iso-Butanol	33.1	35.23	33.01
1-butanol	33.2	35.23	33.01
1-pentanol	34.86	37.02	34.65
1-hexanol	36.05	38.32	35.84
1-heptanol	36.96	39.31	36.74
2-ethyl-1-hexanol	37.64	40.08	37.45
1-octanol	37.69	40.08	37.45
1-nonanol	38.25	40.71	38.02
1-decanol	38.73	41.22	38.49
1-undecanol	39.12	41.65	38.88
1-dodecanol	39.46	42.02	39.22
1-tetradecanol	39.99	42.6	39.75
acids and ester			
methyl formate	14.73	13.64	14.48
methyl acetate	19.73	19.86	19.94
Diethyl malonate	20.11	20.91	21.06
Trimethyl orthoformate	20.89	20.03	19.8
Diethyl carbonate	21.14	21.44	21.33
Ethyl acetoacetate	22.53	22.59	22.57
ethyl acetate	23.43	24.1	23.66
methyl caproate	30.06	31.34	30.02
butyl butanoate	31.2	32.82	31.31
methyl heptanoate	31.36	32.82	31.31
methyl octanoate	32.46	34.03	32.37
decanoic acid	32.97	35.04	33.27
ethyl octanoate	33.28	35.04	33.27
methyl decanoate	34.14	35.91	34.02
ethyl decanoate	34.73	36.65	34.67
methyl laurate	35.36	37.29	35.24
ethyl laurate	35.81	37.86	35.74
methyl myristate	36.31	38.36	36.17
ethyl myristate	36.58	38.8	36.56
methyl linoleate	37.22	38.77	36.75
methyl oleate	37.49	39.34	37.13
ether			
Diethylene glycol	20.33	20.03	19.8
Dioxolane	21.24	19.86	19.94
Triethylene glycol	21.66	21.22	20.93
2-methoxyethanol	22.71	22.55	21.9
Diethylene glycol monomethyl ether	22.9	23.12	22.55
dimethoxymethane	23.29	22.55	21.9
Diethylene glycol dimethyl ether	26.1	25.56	24.72
1.2-dimethoxyethane	26.74	26.28	25.23
dimethyl ether	28.47	28.36	26.73
Diethoxymethane	28.55	29	27.67
Acetal	30.2	31.08	29.53

butylal	33.83	35.13	33.15
diethyl ether	33.84	35.23	33.01
Isopropyl methyl ether	33.85	35.23	33.01
Methyl propyl ether	34.03	35.23	33.01
TAME	36.4	38.32	35.84
tert-Butyl isopropyl ether	37.05	39.31	36.74
dibutyl ether	38.06	40.08	37.45
furanics			
Furfural	23.41	21.25	22.11
Tetrahydrofurfuryl alcohol	26.87	27.18	26.36
Furan	29.33	27.57	27.6
2,3-Dihydrofuran	31.37	30.27	29.51
THF	32.3	32.82	31.31
aldehydes and ketones			
Ethanal	24.51	24.1	23.66
g-Valerolactone	24.73	25.28	25
Cyclohexanone	33.66	34.91	33.46
3-octanone	36.73	38.8	36.56

Table A.4: Raw data of Figure 3.6, ^{a} value derived according to DIN 51900-1 2000 from H_f AFEEFY et al. 2011 and the heat of vaporization JOBACK 1984

substances	L_{st}	$H_{LHV}{}^{a}$ / kJ g^{-1}
hydrocarbons		
Naphthalin	12.9	39.14
biphenyl	12.96	39.36
1-Methylnaphthalene	13.08	39.5
diphenylmethane	13.11	39.76
Benzol	13.23	40.23
1,2-diphenylethane	13.23	40.07
2,6-dimethylnaphthalene	13.23	39.79
Toluol	13.46	40.62
1-n-butylnaphthalene	13.46	40.47
Tetralin	13.55	40.68
cyclooctane	13.63	39.62
ethyl benzene	13.63	41.04
1,3-dimethylbenzene	13.63	40.91
1,3-diethylbenzene	13.86	41.51
sec-butylbenzene	13.86	41.57
n-hexylbenzene	14.01	41.98
n-octylbenzene	14.12	42.24
n-nonylbenzene	14.16	42.34
n-dodecylbenzene	14.26	42.59
n-tetradecylbenzene	14.31	42.71
trans-decalin	14.45	42.69
1,9-decadiene	14.45	44.04
bicyclohexyl	14.5	42.88
cyclohexane	14.74	43.57
methylcyclohexane	14.74	43.49
1,3,5-trimethylcyclohexane	14.74	43.42
n-butylcyclohexane	14.74	43.6
1-hexene	14.74	44.56
1-heptene	14.74	44.44
1-octene	14.74	44.35
2,4,4-trimethyl-1-pentene	14.74	44.03
2-octene	14.74	44.28
1-nonene	14.74	44.29
1-undecene	14.74	44.19
1-tetradecene	14.74	44.1
1-hexadecene	14.74	44.06
1-octadecene	14.74	44.02
9-methylheptadecane	14.89	44.12
heptadecane	14.9	44.15
n-Hexadecane	14.91	44.18
Isohexadecane	14.91	44.04
n-Pentadecane	14.92	44.2
n-Tetradecane	14.93	44.24

n-Tridecane	14.95	44.27
5-butylnonane	14.95	44.28
Dodecane	14.97	44.32
2,2,4,6,6-pentamethylheptane	14.97	44.15
Undecane	14.99	44.36
n-Decane	15.01	44.43
2,2-dimethyloctane	15.01	44.33
n-Nonane	15.04	44.5
2,2,5-trimethylhexane	15.04	44.35
n-Octane	15.08	44.59
n-Heptane	15.13	44.71
2,3-dimethylpentane	15.13	44.63
2,4-dimethylpentane	15.13	44.6
n-Hexane	15.19	44.86
2,2-dimethylbutane	15.19	44.71
3-methylpentane	15.19	44.84
n-Pentane	15.28	45.08
alcohols		
Glycerol	5.24	16.33
Ethylene glycol	5.55	17.32
1.3-Formalglycerol	5.96	18.97
methanol	6.45	20.06
ethanol	8.97	26.99
1-propanol	10.32	30.89
1-butanol	11.15	33.34
iso-Butanol	11.15	33.22
sec-butanol	11.15	33.08
tert-butanol	11.15	32.84
1-pentanol	11.72	34.99
1-hexanol	12.14	36.2
1-heptanol	12.45	37.11
1-octanol	12.7	37.82
2-ethyl-1-hexanol	12.7	37.81
3-octanol	12.7	37.69
1-nonanol	12.9	38.4
1-decanol	13.06	38.87
1-undecanol	13.2	39.28
1-dodecanol	13.31	39.61
palmitoleyl alcohol	13.47	40.39
1-tetradecanol	13.5	40.15
oleyl alcohol	13.6	40.75
1-hexadecanol	13.64	40.57
1-octadecanol	13.76	40.9
acids and ester		
Dimethyl carbonate	4.59	14.46
Trimethyl orthoformate	6.49	20.88
methyl acetate	6.51	19.77
Diethyl malonate	6.88	20.75
Diethyl carbonate	7	21.19
Diethyl maleate	7.2	22.15
Ethyl acetoacetate	7.41	22.44
diethyl succinate	7.52	22.65
2-Ethoxyethyl acetate	7.82	23.96
ethyl acetate	7.82	23.45
Propylene glycol monomethyl ether acetate	7.82	23.92
ethyl levulinate	8.12	24.57
diethyl adipate	8.52	25.58
dibutyl maleate	9.05	27.46
methyl sorbate	9.29	28.88
methyl caproate	10.06	30.1
butyl butanoate	10.51	31.34
methyl heptanoate	10.51	31.43
methyl octanoate	10.89	32.53
decanoic acid	11.2	33.15
ethyl octanoate	11.2	33.36
methyl decanoate	11.47	34.22
butyl octanoate	11.69	34.82
ethyl decanoate	11.69	34.82
trilaurin	11.75	35.02
methyl laurate	11.89	35.47
isopropyl decanoate	11.89	35.32
propyl decanoate	11.89	35.4
octyl valerate	11.89	35.4
acetic acid. dodecyl ester	12.07	35.92
ethyl laurate	12.07	35.92
linolenic acid	12.13	36.81
methyl myristate	12.22	36.42
propyl laurate	12.22	36.37

linolenic acid. methyl ester	12.25	37.32
linoleic acid	12.28	36.99
ethyl myristate	12.36	36.77
tripalmitin	12.38	36.84
methyl linoleate	12.4	37.48
oleic acid	12.44	37.16
triolein	12.45	37.33
methyl palmitate	12.48	37.19
linoleic acid. ethyl ester	12.51	37.72
methyl oleate	12.55	37.64
hexadecyl acetate	12.59	37.47
ethyl palmitate	12.59	37.46
tristearin	12.6	37.5
ethyl oleate	12.65	37.87
methyl stearate	12.7	37.8
isopropyl palmitate	12.7	37.7
octadecyl acetate	12.79	38.03
decyl caprate	12.79	38.03
butyl palmitate	12.79	38.03
ethyl stearate	12.79	38.03
butyl oleate	12.82	38.36
methyl arachidate	12.87	38.31
propyl stearate	12.87	38.27
butyl stearate	12.95	38.5
isobutyl stearate	12.95	38.47
ether		
Diethylene glycol	6.49	20.5
methoxy(methoxymethoxy)methane	6.49	21.14
Dioxolane	6.51	21.21
Triethylene glycol	6.88	21.82
dimethoxymethane	7.24	23.34
2-methoxyethanol	7.24	22.9
Diethylene glycol monomethyl ether	7.46	23.67
triethylene glycol monomethyl ether	7.55	24.02
2.5.7.10-tetraoxaundecane	7.55	24.22
Tetraethylene glycol dimethyl ether	8.06	25.7
Triethylene glycol dimethyl ether	8.12	25.87
2(2-Ethoxyethoxy)ethanol	8.22	25.67
Diethylene glycol dimethyl ether	8.22	26.17
1.2-dimethoxyethane	8.41	26.75
1-methoxy-2 propanol	8.41	25.95
dipropylene glycol monomethyl ether	8.83	27.23
Dipropylene glycol monomethyl ether	8.83	27.23
dimethyl ether	8.97	28.45
tripropylene glycol monomethyl ether	9.02	27.78
Diethoxymethane	9.26	28.59
2-ethoxyethyl ether	9.34	29.04
2-butoxyethanol	9.91	30.22
Acetal	9.91	30.2
1-butoxy-2-propanol	10.42	31.52
diethoxybutane	10.84	32.8
dimethoxyhexane	10.84	33.27
diethyl ether	11.15	33.88
Methyl propyl ether	11.15	34.05
Isopropyl methyl ether	11.15	33.82
butylal	11.18	33.9
TAME	12.14	36.42
tert-Butyl isopropyl ether	12.45	37
2-ethylhexylal	12.64	37.94
dibutyl ether	12.7	38.14
dipentyl ether	13.06	39.13
furanics		
5-HMF	6.56	21.4
Furfural	7.17	23.61
3-Furaldehyde	7.17	23.4
5-(ethoxymethyl)-2-furfural	8.05	25.73
5-Methylfurfural	8.13	26.04
2-Furfuryl methyl ether	8.6	27.59
Tetrahydrofurfuryl alcohol	8.77	27.05
2-(diethoxymethyl)furan	8.91	27.91
Furan	9.11	29.32
furfuryl ethyl ether	9.29	29.28
Methyl tetrahydrofurfuryl ether	9.49	29.53
2,3-Dihydrofuran	9.83	31.14
2-methylfuran	10.07	31.59
THF	10.51	32.38
Dimethylfuran	10.75	33.2

2-Methyltetrahydrofuran	11.2	34.02
aldehydes and ketones		
3-Furaldehyde	7.17	23.4
Ethanal	7.82	24.54
4-Hydroxy-2-butanone	7.82	23.92
Cyclohexanone	11.23	33.77
2-heptanone	12.07	36.05
octanal	12.36	37.14
3-octanone	12.36	36.89

Table A.5: Raw data of Figure 3.7

Substances	L_{st}	H_{LHV} (from H_{LHV} (experimentally) (LIDE 2001) / MJ m^{-3}
hydrocarbons		
1-Methylnaphthalene	13.08	3.89
diphenylmethane	13.11	3.91
Benzol	13.23	3.93
Toluol	13.46	3.9
Tetralin	13.55	3.87
cyclooctane	13.63	3.75
1,3-dimethylbenzene	13.63	3.88
ethyl benzene	13.63	3.89
1,3-diethylbenzene	13.86	3.87
sec-butylbenzene	13.86	3.87
trans-decalin	14.45	3.81
bicyclohexyl	14.5	3.82
methylcyclohexane	14.74	3.81
n-butylcyclohexane	14.74	3.82
cyclohexane	14.74	3.82
1-hexadecene	14.74	3.85
2,4,4-trimethyl-1-pentene	14.74	3.87
2-octene	14.74	3.88
1-octene	14.74	3.89
1-heptene	14.74	3.89
1-hexene	14.74	3.9
heptadecane	14.9	3.82
n-Hexadecane	14.91	3.82
n-Pentadecane	14.92	3.82
n-Tetradecane	14.93	3.82
n-Tridecane	14.95	3.82
Dodecane	14.97	3.82
Undecane	14.99	3.82
n-Decane	15.01	3.82
2,2,5-trimethylhexane	15.04	3.81
n-Nonane	15.04	3.82
n-Octane	15.08	3.82
2,4-dimethylpentane	15.13	3.81
2,3-dimethylpentane	15.13	3.81
n-Heptane	15.13	3.82
2,2-dimethylbutane	15.19	3.8
3-methylpentane	15.19	3.81
n-Hexane	15.19	3.82
n-Pentane	15.28	3.81
alcohols		
Glycerol	5.24	3.97
Ethylene glycol	5.55	3.95
methanol	6.45	4
ethanol	8.97	3.87
1-propanol	10.32	3.85
tert-butanol	11.15	3.8
sec-butanol	11.15	3.82
iso-Butanol	11.15	3.84
1-butanol	11.15	3.85
1-pentanol	11.72	3.84
1-hexanol	12.14	3.84
1-heptanol	12.45	3.84
2-ethyl-1-hexanol	12.7	3.83
1-octanol	12.7	3.84

1-nonanol	12.9	3.83
1-decanol	3.06	3.83
1-undecanol	13.2	3.83
1-dodecanol	13.31	3.83
1-tetradecanol	13.5	3.83
acids and ester		
Methyl formate	4.59	4.15
Trimethyl orthoformate	6.49	4.16
Methyl acetate	6.51	3.92
Diethyl malonate	6.88	3.78
Diethyl carbonate	7	3.91
Ethyl acetoacetate	7.41	3.93
Ethyl acetate	7.82	3.87
Methyl caproate	10.06	3.86
Butyl butanoate	10.51	3.84
Methyl heptanoate	10.51	3.86
Methyl octanoate	10.89	3.85
Decanoic acid	11.2	3.81
Ethyl octanoate	11.2	3.84
Methyl decanoate	11.47	3.85
Ethyl decanoate	11.69	3.84
Methyl laurate	11.89	3.84
Ethyl laurate	12.07	3.84
Methyl myristate	12.22	3.84
Ethyl myristate	12.36	3.83
Methyl linoleate	12.4	3.88
Methyl oleate	12.55	3.86
ethers		
Diethylene glycol	6.49	4.05
Dioxolane	6.51	4.22
Triethylene glycol	6.88	4.07
Furfural	7.17	4.22
2-methoxyethanol	7.24	4.05
Dimethoxymethane	7.24	4.16
Diethylene glycol monomethyl ether	7.46	3.97
Diethylene glycol dimethyl ether	8.22	4.11
1.2-dimethoxyethane	8.41	4.11
Tetrahydrofurfuryl alcohol	8.77	3.96
Dimethyl ether	8.97	4.1
Furan	9.11	4.16
Diethoxymethane	9.26	3.98
2,3-Dihydrofuran	9.83	4.13
Acetal	9.91	3.94
THF	10.51	3.97
Diethyl ether	11.15	3.92
Isopropyl methyl ether	11.15	3.92
Methyl propyl ether	11.15	3.94
Butylal	11.18	3.91
TAME	12.14	3.88
tert-Butyl isopropyl ether	12.45	3.85
Dibutyl ether	12.7	3.87
furanics		
Furfural	7.17	4.22
Tetrahydrofurfuryl alcohol	8.77	3.96
Furan	9.11	4.16
2,3-Dihydrofuran	9.83	4.13
THF	10.51	3.97
aldeyhdes and ketones		
Furfural	7.17	4.22
Ethanal	7.82	4.05
g-Valerolactone	8.26	3.87
Cyclohexanone	11.23	3.87
3-octanone	12.36	3.84

Table A.6: Raw data of Figure 3.7, [a] value derived from H_f (AFEEFY et al. 2011) and the heat of vaporization (JOBACK 1984)

Substances	C/H ratio	CO_2/H_{LHV} [a] [g MJ m^{-1}]
hydrocarbons		
n-Pentane	0.42	67.66
n-Hexane	0.43	68.31
2,2-dimethylbutane	0.43	68.53
3-methylpentane	0.43	68.34
n-Heptane	0.44	68.77
2,3-dimethylpentane	0.44	68.89
2,4-dimethylpentane	0.44	68.94
n-Octane	0.44	69.13
n-Nonane	0.45	69.4
2,2,5-trimethylhexane	0.45	69.63
n-Decane	0.45	69.62
2,2-dimethyloctane	0.45	69.78
Undecane	0.46	69.81
Dodecane	0.46	69.96
2,2,4,6,6-pentamethylheptane	0.46	70.23
n-Tridecane	0.46	70.1
5-butylnonane	0.46	70.08
n-Tetradecane	0.47	70.2
n-Pentadecane	0.47	70.3
n-Hexadecane	0.47	70.39
Isohexadecane	0.47	70.6
heptadecane	0.47	70.47
9-methylheptadecane	0.47	70.55
cyclohexane	0.5	72.01
methylcyclohexane	0.5	72.14
1,3,5-trimethylcyclohexane	0.5	72.27
n-butylcyclohexane	0.5	71.96
1-hexene	0.5	70.41
1-heptene	0.5	70.61
1-octene	0.5	70.74
2,4,4-trimethyl-1-pentene	0.5	71.26
2-octene	0.5	70.86
1-nonene	0.5	70.84
1-undecene	0.5	70.99
1-tetradecene	0.5	71.15
1-hexadecene	0.5	71.21
1-octadecene	0.5	71.27
bicyclohexyl	0.55	74.06
trans-decalin	0.56	74.56
1,9-decadiene	0.56	72.29
n-tetradecylbenzene	0.59	75.09
n-dodecylbenzene	0.6	75.49
n-nonylbenzene	0.63	76.29
n-octylbenzene	0.64	76.64
n-hexylbenzene	0.67	77.53
1,3-diethylbenzene	0.71	79
sec-butylbenzene	0.71	78.89
cyclooctane	0.8	83.71
ethyl benzene	0.8	80.81
1,3-dimethylbenzene	0.8	81.07
Tetralin	0.83	81.83
Toluol	0.88	82.31
1-n-butylnaphthalene	0.88	82.61
Benzol	1	84.03
1,2-diphenylethane	1	84.36
2,6-dimethylnaphthalene	1	84.95
diphenylmethane	1.08	85.53
1-Methylnaphthalene	1.1	86.2
biphenyl	1.2	87.01
Naphthalin	1.25	87.73
alcohols		
1.3-Formalglycerol	0.13	89.13
ethanol	0.17	70.8
1-propanol	0.25	71.11
1-butanol	0.3	71.24
iso-Butanol	0.3	71.49
sec-butanol	0.3	71.78
tert-butanol	0.3	72.32
1-pentanol	0.33	71.34

1-hexanol	0.36	71.39
1-heptanol	0.38	71.44
1-octanol	0.39	71.48
2-ethyl-1-hexanol	0.39	71.51
3-octanol	0.39	71.74
1-nonanol	0.4	71.5
1-decanol	0.41	71.52
1-undecanol	0.42	71.53
1-dodecanol	0.42	71.55
1-tetradecanol	0.43	71.57
1-hexadecanol	0.44	71.59
1-octadecanol	0.45	71.6
palmitoleyl alcohol	0.47	72.51
oleyl alcohol	0.47	72.42
acids and ester		
Trimethyl orthoformate	0.1	79.46
methyl acetate	0.17	90.15
Diethyl carbonate	0.2	87.91
Diethyl malonate	0.25	92.71
2-Ethoxyethyl acetate	0.25	83.38
ethyl acetate	0.25	85.21
Propylene glycol monomethyl ether acetate	0.25	83.53
diethyl succinate	0.29	89.23
Ethyl acetoacetate	0.3	90.42
ethyl levulinate	0.33	86.95
diethyl adipate	0.33	85.07
Diethyl maleate	0.33	92.31
methyl caproate	0.36	78.61
butyl butanoate	0.38	77.9
methyl heptanoate	0.38	77.67
methyl octanoate	0.39	76.96
decanoic acid	0.4	77.08
dibutyl maleate	0.4	84.24
ethyl octanoate	0.4	76.57
methyl decanoate	0.41	75.95
butyl octanoate	0.42	75.72
ethyl decanoate	0.42	75.72
methyl laurate	0.42	75.26
isopropyl decanoate	0.42	75.57
propyl decanoate	0.42	75.39
octyl valerate	0.42	75.39
acetic acid. dodecyl ester	0.43	75.11
ethyl laurate	0.43	75.12
methyl myristate	0.43	74.77
propyl laurate	0.43	74.88
ethyl myristate	0.44	74.67
methyl palmitate	0.44	74.39
hexadecyl acetate	0.44	74.32
ethyl palmitate	0.44	74.33
trilaurin	0.45	76.69
methyl stearate	0.45	74.1
isopropyl palmitate	0.45	74.31
octadecyl acetate	0.45	74.05
decyl caprate	0.45	74.06
butyl palmitate	0.45	74.06
ethyl stearate	0.45	74.06
methyl arachidate	0.45	73.87
propyl stearate	0.45	73.95
butyl stearate	0.45	73.84
isobutyl stearate	0.45	73.89
tripalmitin	0.46	75.46
tristearin	0.46	75.04
oleic acid	0.47	75.48
methyl oleate	0.47	74.93
ethyl oleate	0.47	74.84
butyl oleate	0.48	74.55
triolein	0.49	75.89
methyl sorbate	0.5	84.57
linoleic acid	0.5	76.37
methyl linoleate	0.5	75.76
linoleic acid. ethyl ester	0.5	75.64
ether		
Diethylene glycol	0.1	80.9
methoxy(methoxymethoxy)methane	0.1	78.49
dimethoxymethane	0.13	74.33
2-methoxyethanol	0.13	75.75
Triethylene glycol	0.14	80.6

dimethyl ether	0.17	66.15
Dioxolane	0.17	84.02
Diethylene glycol monomethyl ether	0.17	77.39
triethylene glycol monomethyl ether	0.19	78.12
2.5.7.10-tetraoxaundecane	0.19	77.46
1.2-dimethoxyethane	0.2	73.03
1-methoxy-2 propanol	0.2	75.27
2(2-Ethoxyethoxy)ethanol	0.21	76.68
Diethylene glycol dimethyl ether	0.21	75.21
Triethylene glycol dimethyl ether	0.22	76.36
Tetraethylene glycol dimethyl ether	0.23	77.05
dipropylene glycol monomethyl ether	0.25	76.35
Dipropylene glycol monomethyl ether	0.25	76.35
Diethoxymethane	0.25	73.89
tripropylene glycol monomethyl ether	0.27	76.79
2-ethoxyethyl ether	0.28	74.72
2-butoxyethanol	0.29	73.95
Acetal	0.29	73.99
diethyl ether	0.3	70.1
Methyl propyl ether	0.3	69.74
Isopropyl methyl ether	0.3	70.23
1-butoxy-2-propanol	0.31	73.93
diethoxybutane	0.33	73.41
dimethoxyhexane	0.33	72.36
butylal	0.35	72.91
TAME	0.36	70.96
tert-Butyl isopropyl ether	0.38	71.64
dibutyl ether	0.39	70.89
dipentyl ether	0.41	71.06
2-ethylhexylal	0.42	72.37
furanics		
Tetrahydrofurfuryl alcohol	0.3	79.67
Methyl tetrahydrofurfuryl ether	0.33	76.99
THF	0.38	75.41
2-Methyltetrahydrofuran	0.4	75.1
2-(diethoxymethyl)furan	0.43	83.37
5-HMF	0.5	97.83
2-Furfuryl methyl ether	0.5	85.37
furfuryl ethyl ether	0.5	83.41
2,3-Dihydrofuran	0.5	80.66
5-(ethoxymethyl)-2-furfural	0.5	88.75
Dimethylfuran	0.63	82.75
2-methylfuran	0.67	84.85
5-Methylfurfural	0.67	92.1
Furfural	0.75	97.01
Furan	0.75	88.21
3-Furaldehyde	0.75	97.87
aldehydes and ketones		
Ethanal	0.25	79.53
4-Hydroxy-2-butanone	0.25	83.52
2-heptanone	0.43	74.83
octanal	0.44	73.93
3-octanone	0.44	74.45
Cyclohexanone	0.5	79.67
3-Furaldehyde	0.75	97.87

Table A.7: Raw data of Figure 3.8, measurements at Institute of Internal Combustion Engines, TU Braunschweig

evaporated volume [%]	temperature [°C]					
	Swedish class 1 diesel	US diesel	Fisher-Tropsch-diesel	B10	B100	kerosine
0	184	198.7	218.6	164	330	153
2					350	
5	197.8	216.3	240.4	190	353	
10	203.4	221.2	244.6	200	354	166
20	210.4	229.6	257.1	217		
30	218	239.6	268.8	234		
40	226.1	249.7	282	250		
50	233.5	258.8	294.8	268	355	177
60	242	266.2	307	285		
70	250.2	273.8	317.8	302		
80	259.1	282.7	329	318		
90	270.5	295.6	344.3	330		247
95	279.9	308.4	356.4	350.1		
100	290	320.2	359.6		360	283

Table A.8: Raw data of Figure 3.8 derived from LIDE 2001

pure substances	boiling point [°C]
n-hexadecane	287

A.2 Particle Distribution Emulsion

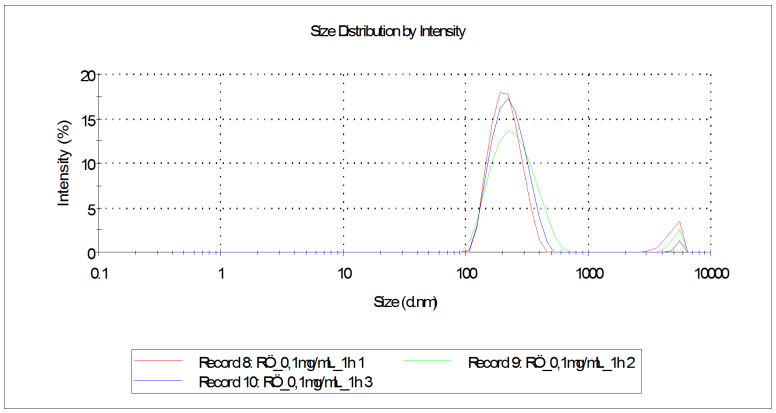

Figure A.1: light scatter measurement for an emulsion of rapeseed oil

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